12-1-1980

Removal of Sodium from Lignite by Ion Exchange in a Continuous Countercurrent Unit

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REMOVAL OF SODIUM FROM LIGNITE BY ION EXCHANGE IN A CONTINUOUS COUNTERCURRENT UNIT

by
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Bachelor of Science, Chemical Engineering
University of North Dakota, May 1979

A Thesis

Submitted to the Graduate Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the degree of

Master of Science

Grand Forks, North Dakota

December
1980

This thesis submitted by Solomon Bekele in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota is hereby approved by the Faculty Advisary Committee under whom the work has been done.

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This thesis meets the standards for appearance and conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

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Department Chemical Engineering

Degree Master of Science

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Signature Solomon Bekele

Date Sept 4, 1980

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ACKNOWLEDGEMENTS

I wish to express my gratitude to the Chemical Engineering Department, University of North Dakota, and to the Grand Forks Energy Technology Center for the grant of Graduate Teaching Assistantship and Graduate Research Assistantship which made this work possible.

Sincere and special thanks are due to Dr. Dorab N. Baria for his supervision and guidance throughout this project. I would like to take this opportunity to thank Professor Wayne R. Kube and Dr. Milton E. Winger for serving on the Thesis Committee.

Technical assistance given by Reid Lamppa, Brad Esckilson and Jaime O'Toole is gladly appreciated.

I must express my sincere gratitude and appreciation to Mrs. Deanne H. Nelson for having typed the draft of this thesis in the nick of time. I also thank Mrs. Anita Paulsen for typing this thesis.

Finally, I wish to acknowledge a great debt of love and gratitude to my wife, Atalfim Mengistu, for her constant encouragement throughout this project.

ABSTRACT

The exchange of sodium and other cations from lignite by hydrogen ion in an aqueous H_2SO_4 medium was investigated in a continuous countercurrent ion exchange unit. This was studied as a function of solid residence time, solid/liquid mass ratio, initial acid concentration and lignite particle size.

Cations removal from lignite increased with an increase in residence time and in acid concentration and with a decrease in solid/liquid mass ratio and in particle size. The removal of sodium reached equilibrium values at 50 minutes residence time and for 0.4651 N solution concentration. Solid/liquid mass ratios of less than 1/2 produced no significant increase in sodium removal. Particle sizes of less than 35 mesh were not required to reduce the sodium content of the lignite to less than 5 percent of its initial content.

A theoretical model featuring film diffusion control was postulated for the removal of sodium from lignite. The experimental data were consistent with this model. An overall empirical correlation, based on the film diffusion model, relating the percent sodium removed from lignite, Y, to the solid residence time t, seconds, solid/liquid mass ratio P, initial acid concentration C, normality, and particle size r_o, centimeters, was obtained using a linear least-squares regression.

$$Y = \exp \frac{-0.160 t^{0.316} C^{0.259}}{p^{0.241} r_o^{0.274}}$$

The least-squares fit had a multiple correlation coefficient of 0.860. Partial F statistics indicated that the heirarchy of the independent variables in predicting the dependent variable is acid concentration, solid residence time, particle size and solid/liquid mass ratio in decreasing contribution.

I. INTRODUCTION

Coal supplied 19 percent of the total energy used in the United States in 1977 and estimates are that coal will meet 38 percent of the total projected energy demand by the year 2000 (1). The technology exists to mine, move and use this abundant and relatively inexpensive fuel in environmentally acceptable ways to meet this demand.

Lignite deposits of North Dakota constitute about 22 percent by weight of the total explored and mapped coal resources of the United States. On a heating value basis, North Dakota lignite accounts for 18 percent of the total energy in the coal reserves (2). Open pit mining and the relative ease in reclaiming the mined area makes expanded use of lignite attractive. Steam boilers employed in the generation of electric power are major users of lignite.

As the use of lignite for power generation has increased drastically over the years, a serious problem in fire-side ash fouling of boiler heat-transfer surfaces has been encountered. Ash fouling obstructs gas flow in boiler passes, reduces heat transfer, lowers efficiency and causes hot spots (2,3,4). Previous studies indicate that ash fouling varies from one lignite-fired boiler to another and depends on various factors such as boiler design, load factor, excess air, tube metal temperatures, and the characteristics of the lignite ash (4). Other factors being equal, the degree and rate of ash fouling is directly proportional to the sodium content of the lignite (5,6,7). It has been observed from pilot plant tests that lignites containing greater than 4 percent Na_2O in the ash tend to be medium or high fouling (8).

Some of the methods and alternatives tried or suggested to reduce and minimize ash fouling in pulverized-coal fired boilers include:

(a) burning low sodium lignite; (b) blending low and high sodium lignites; (c) using chemical additives in the lignite to mask the effect of sodium; (d) incorporating special design features and cleaning devices in the boiler; (e) oversizing heating surfaces to accomodate some fouling; (f) cleaning the lignite chemically or physically before combustion; and (g) using additives, like limestone, in the lignite to break up ash build-up on boiler tubes (3,6,7,8).

Lignite in North Dakota containing less than 4 percent Na_2O in the ash accounts for only a third of the total lignite reserve. There is also a great variability of lignite ash within and between mines (7,9). Hence, it is unlikely that steps (a) and (b) will be viable in the long term. Chemical additives have not been found effective in reducing fouling significantly (6). Design modifications or incorporation of cleaning units will increase the initial cost of the boiler and do not necessarily prevent the problem completely. Additives like limestone have had partial success in breaking up the ash buildup.

Most of the sodium, potassium, calcium and magnesium associated with lignite are present in the organic structure as salts of humic acid (2,5,8,10). These metals can be removed from the lignite by exchanging them with other ions. Removal of sodium by ion exchange is thus a potential option to minimize fire-side tube fouling in boilers.

The purpose of the present investigation is to study the feasibility of removing sodium and other ions from the lignite by H^+ in aqueous H_2SO_4 solution using a continuous countercurrent unit. This was studied as a function of the solid residence time, initial acid concentration, solid particle size and solid/liquid mass ratio.

II. PREVIOUS EXPERIMENTAL WORK

The exchange of sodium from lignite by various ions has been investigated previously in batch (5,10,11) and continuous (8) systems. In batch systems, the lignite was treated with aqueous solution of an electrolyte for a given contact time. In continuous systems, the lignite and the electrolyte solution were contacted in a countercurrent manner.

Many coals, including lignite, act as cation exchangers since they contain carboxylic and possibly other weak-acid groups. Sodium, potassium, calcium, magnesium and to a lesser extent aluminum and iron exist in lignite as salts of carboxylic or humic acids, and hence are exchangeable since they ionize in aqueous solutions. Exchange ions from aqueous solutions can diffuse through the pores and capillaries of lignite to replace sodium and other cations present in the lignite. The ease of replacement of the cations on the lignite was found to be: $Na^{+} > K^{+} > Mg^{++} > Ca^{++} > Al^{+++} > Fe^{+++} > H^{+}$ (10,12,13). This is as expected according to their size and valence, except for H^{+}. Hydrogen ion has a marked attraction for the oxygen atom of the carboxyl group and is difficult to exchange (22). The other cations form strong electrolytes with carboxyl group and do dissociate and are easily replaced by hydrogen and other cations

Calcium, magnesium, iron, aluminum and hydrogen were the principal cations used in ion exchange studies to remove Na^{+} from lignite, hydrogen being by far the most effective. The relative efficiency of exchange cations increased with increase in the positive charge, H^{+} being the most efficient. Monovalent ions were replaced readily by divalent and

trivalent ions and likewise divalent ions were replaced easily by trivalent ions (10).

Previous batch studies on the ion exchange of sodium from lignite used distilled water, tap water and various aqueous electrolyte solutions (5,10,11). Residence time, particle size, solution concentration, liquid to lignite mass ratio, and moisture content of the lignite were the variables studied. Some of the results of these studies were: (a) sodium was the easiest cation to replace in the lignite; (b) ionic solutions were more effective than distilled water in removing sodium indicating that sodium in the lignite was not water-soluble; (c) for near complete exchange of the sodium a solution concentration greater than 0.5 ionic strength was not needed, even for high sodium lignites; (d) the exchange of sodium was most effective with small particle sizes; (e) neither increasing the liquid to lignite ratio nor prolonging the residence time were very effective in increasing the removal of sodium once apparent equilibrium was attained; and (f) for moisture content of less than 20 percent, the rate of sodium removal was extremely slow due to size contraction and permanent pore size reduction.

The effectiveness of solid residence time, solution concentration, different cations, liquid to lignite ratio, particle size, lignite moisture content and recycling of spent solution in the removal of sodium from lignite were investigated in a continuous countercurrent system (8). Various salts and oxides of calcium and dilute concentrations of H_2SO_4 were used. Results from this investigation support the findings of the batch systems. Among the solutions studied, H_2SO_4 and $CaCl_2$ were found to be the two most effective (8). Successive recycling of the spent solution rapidly reduced the sodium removal as more and more

sodium was added to the lignite by exchanging with other cations present in the lignite.

III. GENERAL OVERVIEW OF ION EXCHANGE

A. HISTORICAL ACCOUNT

In the early part of the nineteenth century, Sir Humphrey Davy and others studied the ability of clays and other soils in adsorbing the soluble components of manure liquors (14). Ion exchange received scientific recognition in 1850 when H.S. Thompson and J.H. Way, English soil chemists, rediscovered ion exchange in soils. They discovered independently that when a soil was treated with either $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$, most of the ammonia was adsorbed and calcium was released into the solution (15). Though Thompson and Way are credited for the discovery of the phenomenon of ion exchange, in 1833 Fuchs reported that certain clays released potassium and sodium when treated with lime and Graham found that carbon adsorbed silver from a solution of $AgNO_3$ (14).

In 1876 Lemberg identified clays, zeolites, glauconites and humic acids as materials useable for ion exchange (16). Attempts followed Lemberg's work to use these materials in water softening and to synthesize products with similar properties.

Harm and Rumper prepared the first synthetic industrial ion exchange in 1903. Until 1935 when Adams and Holmes developed synthetic organic exchangers in England, ion exchange was used on an industrial scale solely for water softening (15). The improved properties of synthetic organic exchangers and advanced ion exchange technology are responsible for establishing ion exchange as a unit operation.

B. BASIC PRINCIPLES OF ION EXCHANGE

Ion exchangers are insoluble solids which carry exchangeable positive or negative ions. When an ion exchanger is in contact with an electrolytic solution there will be a reversible exchange of stoichiometrically equivalent ions between the exchanger and the solution. Cation exchangers are capable of exchanging cations or positively charged ions while anion exchangers are capable of exchanging anions or negatively charged ions. Many substances including phosphates, humus, cellulose, protein, carbon, resins, coals, living cells and many minerals exhibit the property of ion exchange.

Ion exchange is generally a reversible process. A cation exchange that has been depleted can be regenerated by contact with a solution of the cation. Ion exchange is also stoichiometric, that is, for every equivalent of the exchanging ion taken up by the exchanger, an equivalent is released from the exchanger (15).

Many coals contain carboxylic and other weak acid groups. Attached to the carboxylic acids in the form of salts are alkaline metals such as sodium, calcium and magnesium. These metals are ion exchangeable when the coal is in contact with an aqueous electrolytic solution. Thus, coals like lignite serve as cation exchangers with or without being treated with solutions of different salts to stabilize them before use (16).

Both natural and synthetic exchangers are used today. The most common and important ones include ion exchange resins, ion exchange coals, mineral ion exchangers, and synthetic inorganic ion exchangers (14). All possess the same general structural framework but each has its own unique behavior. Among numerous industrial uses

of ion exchange, the two foremost are water treatment and chemical processing.

IV. KINETICS OF ION EXCHANGE

A. MECHANISM OF ION EXCHANGE

The design and sizing of ion exchange equipment require data pertaining to the ion exchange kinetics, an area that is not well developed and confined almost exclusively to simple ideal systems. Ion exchange is basically a diffusion process, and the basic mechanism is a redistribution of an equivalent amount of counter ions by diffusion (18). Counter ions are those ionic species that move from the ion exchanger into the solution and vice versa. Electro-neutrality restricts counter ion diffusion and is preserved when charge transfer by counter ion A is balanced by equivalent charge transfer by counter ion B.

B. RATE CONTROLLING STEPS

Lignite has a porous structure and acts as a cation exchanger. During ion exchange there will be a two-way diffusion in the lignite and the aqueous electrolytic solution. The ion exchange process can be broken up into the following steps: (a) diffusion of exchange ion from the bulk of the liquid to the external surface of the solid exchanger particle; (b) diffusion of exchange ion through the pores and capillaries of the solid particle to the site of exchange; (c) exchange of ions; (d) diffusion of the released ions to the surface of the solid through the pores and capillaries of the particle and (e) diffusion of the released ions from the surface of the solid to the bulk of the liquid (17). Reaction at the solid surfaces /step (c)/ is extremely rapid and the resistance due to this step will generally be negligible (18,19). The potential rate-determining

steps are external (film) diffusion involving steps (a) and (e) and internal (particle) diffusion involving steps (b) and (d). Film diffusion occurs essentially in an adherent stagnant liquid boundry layer for mass transfer while particle diffusion takes place within the pores and capillaries of the particle.

In ideal film diffusion control, concentration gradients occur in the liquid film as particle diffusion is faster than film diffusion. Conversely, in ideal particle diffusion controlling mechanism, concentration gradients develop in the particle since diffusion in the film is very rapid. As film and particle diffusion follow each other, the slower of the two is rate-controlling. Both rate-controlling steps are governed by exchanger properties and by operating conditions. A dimensionless modules developed by Helfferich theoretically predicts the rate-controlling step (20):

$$\frac{\bar{C}D\delta}{CDr_o}(5 + 2\alpha_{A/B}) \ll 1 \quad \text{particle-diffusion control} \qquad (1)$$

$$\gg 1 \quad \text{film-diffusion control} \qquad (2)$$

$$\doteq 1 \quad \text{intermediate} \qquad (3)$$

where $\bar{C}$ = concentration of fixed ionic groups in lignite, meq/cm^3;

C = bulk concentration of solution, meq/cm^3;

$\bar{D}$ = interdiffusion coefficient in the particle, cm^2/sec;

r_o = particle radius, cm;

δ = film thickness, cm;

and $\alpha_{A/B}$ = separation of factor, dimensionless.

Separation factor is the preference of the ion exchanger for one of the two counterions.

The experimental method for distinguishing between particle and film diffusion is the "interruption test," in which diffusion is briefly stopped by removing the particles from the solution (20). With particle diffusion control the exchange rate is higher upon reimmersion since internal concentration gradients have had time to level out. Helfferich (19) outlines some of the general rules for the dependence of the ion exchange rate on various factors.

RATES OF ION EXCHANGE

The kinetics of liquid-solid ion exchange are generally described by either empirical rate equations or fundamental diffusion equations. Most of these equations are applicable only to binary batch systems, although their modifications under ideal limiting conditions are applicable to multicomponent semi-continuous and continuous systems. The theoretical treatment of ion exchange kinetics assumes the ion exchanger to be a quasi-homogeneous phase in order to bypass the inhomogeniety in the molecular and geometrical structure of the ion exchanger (20). The prediction of the rate of ion exchange involves solving the differential diffusion equations for a homogeneous phase under appropriate boundary conditions.

Fick's first law with a constant interdiffusion coefficient can be used to describe a particle diffusion and a film diffusion control process (20):

$$\bar{J}_A = -\bar{D} \text{ grad } \bar{C}_A \qquad \text{particle diffusion} \qquad (4)$$

$$J_A = D\Delta C_A/\delta \qquad \text{film diffusion} \qquad (5)$$

where J_A = the mass flux of the diffusing species A, mmoles/cm^2/sec;

C_A = concentration of species A; meq/cm^3;

and ΔC_A = concentration difference between the boundaries of the film, meq/cm^3.

Quantities with bars refer to the interior of the exchanger. This approach is valid for isotopic exchange in equilibrium and for ion exchange of counter ions of equal mobility. Equation 5 assumes diffusion across the film is quasi-stationary and one dimensional.

The Nernst-Planck equation takes into account the electrical potential gradients, and relates the mass flux J_A of species A to its concentration C_A, the electric potential φ (ergs/coulomb) and the chemical valence Z_A according to the following equation (20):

$$\bar{J}_A = -\bar{D}_A \left(\text{grad } \bar{C}_A + Z_A \bar{C}_A \frac{F}{RT} \text{ grad} \varphi\right) \tag{6}$$

where F = Faraday constant, coulomb/mole;

R = gas constant, erg/mole/deg;

and T = absolute temperature, degrees.

For particle diffusion control with the assumptions, (a) that the total counter ion concentration must remain constant and equal to the concentration of the fixed ionic groups and, (b) that the fluxes of the counter ions A and B in the opposite directions must equal in magnitude (18), the Nernst-Planck equations for A and B can be combined to obtain:

$$\bar{J}_A = -\bar{D} \text{ grad } \bar{C}_A \tag{7}$$

where

$$\bar{D} = \frac{\bar{D}_A \bar{D}_B (Z^2_A \bar{C}_A + Z^2_B \bar{C}_B)}{Z^2_A \bar{C}_A \bar{D}_A + Z^2_B \bar{C}_B \bar{D}_B} \tag{8}$$

Equation 7 reduces to 4 when the ions are of equal mobility or when the concentration of one counter ion is very much smaller than the

other. The interdiffusion rate is thus controlled by the ion which is in the minority as $\bar{D}$ assumes the value of $\bar{D}_A$ for $\bar{C}_A \ll \bar{C}_B$ and that of $\bar{D}_B$ for $\bar{C}_B \ll \bar{C}_A$.

In limiting ideal systems where film diffusion is rate controlling, the diffusion coefficient can be assumed to be constant (20).

The flux equations with the continuity condition give the time dependence of concentration for particle diffusion and film diffusion control for a spherical geometry as follows (23):

$$\frac{\partial \bar{C}_A}{\partial t} = \bar{D} \left(\frac{\partial^2 \bar{C}_A}{\partial r^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} \right) \tag{9}$$

$$-\frac{dC'_A}{dt} = \frac{3C\ J_A}{r_o \bar{C}} \tag{10}$$

where r = distance from particle center, cm;

C'_A = concentration at ion exchanger - film interface, meq/cm^3;

and $C = C_A + C_B$, meq/cm^3.

The solutions of equation 9 and 10 under the infinite solution volume condition are equations 11 and 12, respectively (20).

$$\bar{F}(t) = \left[\bar{1} - \exp \left(-\bar{D}t\, \pi^2 / r_o^2 \right) \right]^{1/2} \tag{11}$$

$$F(t) = 1 - \exp \left(-3DC\ t / r_o \delta \bar{C} \right) \tag{12}$$

The fractional attainment of equilibrium F(t) is the amount of counter ion left in an ion exchanger when equilibrium is reached.

The time required to achieve 50 percent conversion by ion exchange, $t_{1/2}$, calculated from equations 11 and 12 are:

$$t_{1/2} = \frac{0.030\ r_o^2}{\bar{D}} \tag{13}$$

$$t_{1/2} = \frac{0.23\ r_o \delta \bar{C}}{DC} \tag{14}$$

In particle diffusion control the relative rate of exchange is seen to be directly proportional to the interdiffusion coefficient and inversely proportional to the square of the particle radius. The relative rate of exchange in film diffusion control varies directly with the diffusion coefficient and the concentration of the solution and inversely with the particle radius, the film thickness and the counter ion concentration in the particle.

The film thickness can be approximated by the following empirical relation (20):

$$\delta = .20 r_o/(1 + 70 r_o \upsilon) \tag{15}$$

where υ = liquid flow rate/cross sectional area, cm/sec. This approximation is for columns with spherical ion exchangers and for low flow-rates.

The fractional attainment equations are convenient to use but should be used carefully considering the assumptions upon which their derivations are based. For ion exchangers with selectivity and ions of different mobilities, the instantaneous rate of overall ion exchange process can be approximated by empirical equations which assume a linear driving force relation (18,21).

V. EQUIPMENT, TEST AND ANALYSES

A. EQUIPMENT DESCRIPTION AND OPERATIONAL PROCEDURES

The countercurrent ion exchange unit consisted of a carbon steel auger 2-1/8 inches in diameter mounted inside an inclined hollow plastic tube 15 inches long. The auger moved the lignite through the hollow tube. Lignite from a small hopper was fed by a metered feed auger through a vertical tube into the lower part of the ion exchange unit. Dilute H_2SO_4 was introduced through one of four outlets along the hollow tube. Lignite and solution were contacted in a countercurrent manner. Figure 1 is a schematic drawing of the ion exchange unit.

The number of auger revolutions between the inlets of the lignite and H_2SO_4 solution times the period of rotation of the auger that moved the lignite through the hollow tube defines the residence time. By varying the rotation of the auger and keeping all other experimental conditions constant, residence times of 10.22, 20.44, 51.1 and 102.2 minutes were obtained.

The lignite feed rate remained at 12.13 g/min while the solution flow rate varied from 12.06 ml/min to 48.56 ml/min to obtain solid/liquid mass ratios of 1/1, 1/2, 1/3 and 1/4.

Processed lignite and spent solution were discharged at the upper and lower ends of the hollow tube, respectively. The processed lignite was then filtered, washed with distilled water and dewatered on a Buchner funnel. The spent solution was also filtered to separate the fine lignite carry-overs from the effluent. Samples were collected at 10 and 20 minutes to ensure steady state operation.

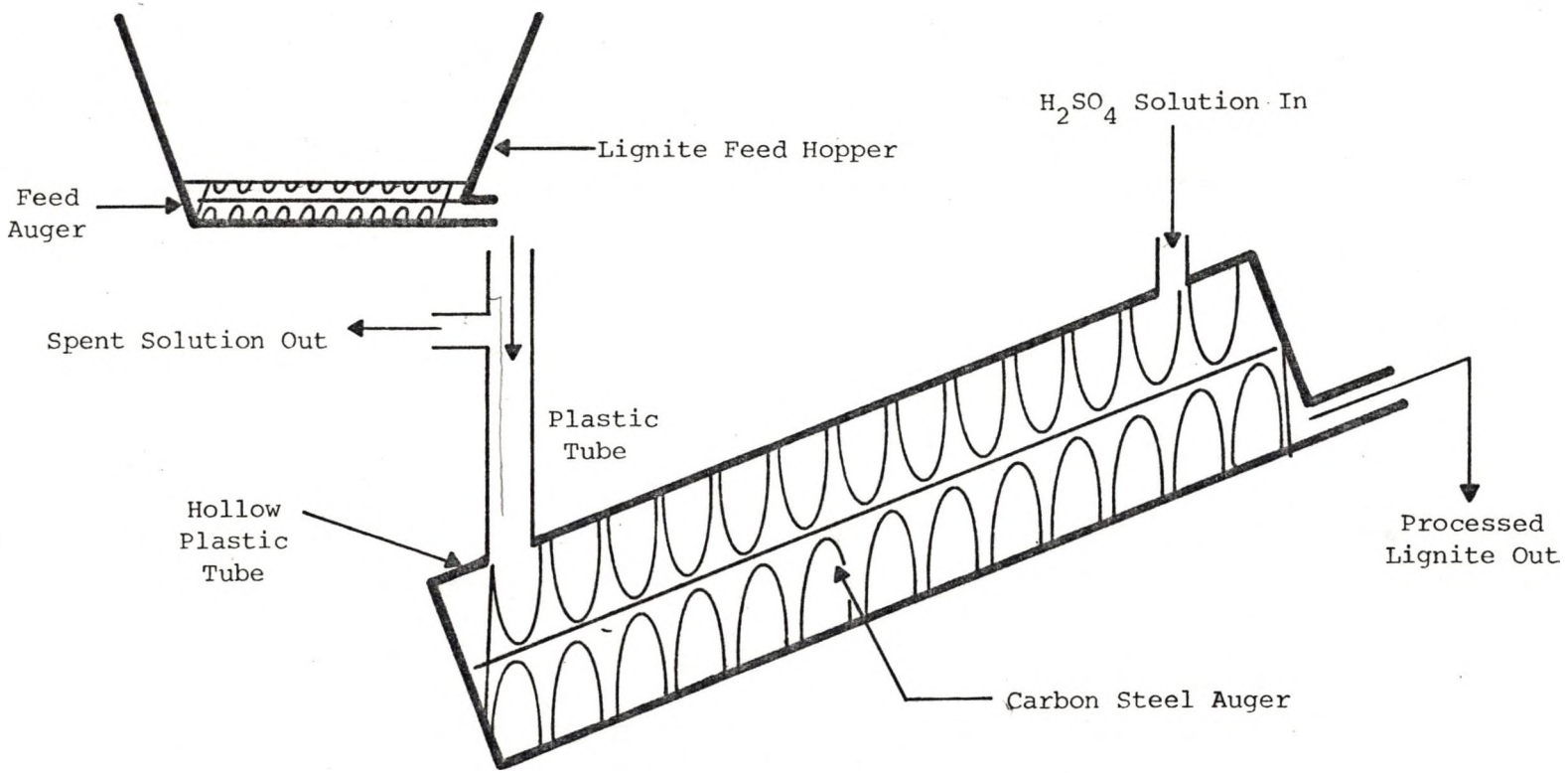

FIGURE 1 - SCHEMATIC OF ION EXCHANGE UNIT

Some samples were run in duplicates to insure that the data was reproducible.

B. STANDARD TEST METHODS

The size distribution of the lignite was determined using a CENCO-MEIZNER Sieve shaker with a bracket. A sample was weighed into the top of a sieve screen deck and agitated through a series of sieve screens of mesh size 10 and 48 Tyler Scale for about ten minutes. The sieve screens were weighed at the end of the agitation period and the weight percent of lignite passing and on each sieve was computed.

Standard ASTM procedures were used to prepare and standardize H_2SO_4 solutions and to analyze "as received" and dewatered processed lignite for moisture and ash. The pH of effluent solutions was measured with a Beckman Zeromatic pH meter.

The lignite ash was analyzed for the inorganic constituents by a standard procedure. A 0.1 g of sample of ash and 0.6 g of $LiBO_2$ were weighed and mixed in a graphite crucible. After careful mixing, the crucible was placed in a muffle furnace and heated slowly until the temperature reached 1790^{o}F. After 15 more minutes of firing, the fused sample was allowed to cool and form a pellet. The pellet then was dissolved in 40 ml of 8/1 distilled water/HNO_3 solution. After dissolution the solution was diluted with distilled water to 100 ml.

This solution was analyzed for sodium, potassium, magnesium, calcium and aluminum by Atomic Absorption Spectroscopy (AA). A Perkin-Elmer model 303 Atomic Absorption Spectrophotometer equipped with Perkin-Elmer model 303 Burner Regulator supplying C_3H_8, C_2H_2,

N_2O and air, and a model DCR1 Concentration Readout were used. The effluent solution was also analyzed by AA technique for the same elements.

Appropriate standards were prepared by dilution from 1000 parts per million (ppm) reference standards. The operation and procedure utilized for AA were standard manufacturer's recommended procedure (23).

C. ANALYSIS OF TEST LIGNITE

The lignite used for this project was obtained from the South Mine of the Knife River Coal Mining Company, Beulah, North Dakota. Proximate analysis of this lignite is given in Table 1. Percent fixed carbon and volatile matter are determined by difference. Table 2 contains the ash analysis of the lignite. Size distribution of the lignite screened between -10 mesh and +48 mesh Tyler Scale is given in Table 3.

TABLE 1 - PROXIMATE ANALYSIS OF AS-RECEIVED LIGNITE

	%
Moisture	28.7
Ash	9.5
Fixed carbon and volatile matter	61.8
	100.0

TABLE 2 - ASH ANALYSIS OF LIGNITE[a/]

	%
Na_2O	9.2
K_2O	0.4
CaO	20.7
MgO	5.2
Al_2O_3	11.5
Fe_2O_3	10.0
TiO_2	0.4
SO_3	24.2
P_2O_5	0.7
SiO_2	17.7
Total	100.0

[a/] Normalized averages

TABLE 3 - SIZE ANALYSIS OF AS-RECEIVED LIGNITE

Size, mesh[b/]	%
+10	.1
-10 x +14	19.0
-14 x +20	24.4
-20 x +28	21.8
-28 x +35	17.6
-35 x +48	17.1

[b/] Tyler Scale

VI. RESULTS AND DISCUSSION

A. GENERAL

Experiments were performed varying (a) solid residence time from 10.22 to 102.2 minutes; (b) solid/liquid mass ratio from 1/1 to 1/4; (c) initial H_2SO_4 concentration from 0.04131 N to 0.8092 N; and (d) solid particle size from -10 mesh to +48 mesh (Tyler Scale). All tests were performed at an average ambient temperature of 23°C. The results, which include the percent of the various cations remaining in the processed lignite, the composition of the effluent solution, and the material balance closures, are tabulated in Tables 4 to 7 respectively for each of the above variables.

The effluent solution from the ion exchange unit contained, on the average, about 10 percent of the original lignite carried over as fines. The mass ratio of carry-over solids/effluent solution for most runs averaged 1/65. The pH of the effluent solution was greater than 4, except in two cases where the H_2SO_4 concentration was greater than 0.1118 N. This indicated negligible free H^+ in the effluent.

Raw data obtained for varying solid residence time, solid/liquid mass ratio, initial H_2SO_4 concentration and solid particle size is indicated in Tables A-1 to A-4 respectively in Appendix A. They include percent moisture-free (MF) ash, the ppm of the cations in the moisture-ash-free (MAF) coal and the percent metal oxides in the ash.

The percent cation remaining in lignite after ion exchange was calculated as the ratio of the mass of cation in the processed

TABLE 4- ANALYSIS OF LIGNITE AFTER ION EXCHANGE AND COMPOSITION OF EFFLUENT SOLUTION FOR VARYING RESIDENCE TIME

Particle Size Range = -10 x +48 mesh
Solid/Liquid Mass Ratio = 1/2
Concentration of Input H_2SO_4 = 0.1118 N.

Residence Time	Percent		Percent Cation Remaining In Lignite After Ion Exchange (MAF)					Effluent Concentration In ppm and pH						Material Balance, Percent				
Minutes	Moisture	Ash (MF)	Na	K	Mg	Ca	Al	Na	K	Mg	Ca	Al	pH	Na	K	Mg	Ca	Al
10.22	40.0	6.1	23.9	36.1	76.7	83.5	100.0	1750	19.0	175	340	0	5.7	88.6	46.2	92.8	90.3	84.0
20.44	40.3	5.2	12.4	23.5	45.1	65.7	100.0	1950	16.8	172	367	0	5.5	87.7	59.1	97.8	91.2	94.8
51.1	41.7	7.4	4.9	16.7	36.0	48.5	100.0	2270	13.0	233	600	0	6.1	91.5	36.3	71.5	75.8	94.2
102.2	38.6	5.6	4.1	13.0	24.3	35.9	82.8	2500	13.0	450	950	1.0	4.9	95.7	20.2	68.5	55.3	82.9

TABLE 5- ANALYSIS OF LIGNITE AFTER ION EXCHANGE AND COMPOSITION OF EFFLUENT SOLUTION FOR VARYING SOLID/LIQUID MASS RATIO

Particle Size Range = -10 x +48 mesh
Residence Time = 20.44 minutes
Concentration of Input H_2SO_4 = 0.1118 N.

Solid/Liquid Mass Ratio	Percent		Percent Cation Remaining In Lignite After Ion Exchange (MAF)					Effluent Concentration In ppm and pH						Material Balance, Percent				
	Moisture	Ash (MF)	Na	K	Mg	Ca	Al	Na	K	Mg	Ca	Al	pH	Na	K	Mg	Ca	Al
1/1	43.0	8.6	18.7	21.8	47.5	69.6	100	1843	16	169	329	0	5.6	60.0	40.4	71.6	88.9	93.4
1/2	40.3	5.2	12.4	23.5	45.1	67.6	100	1752	14	155	422	1	5.5	87.7	59.1	97.8	91.2	94.8
1/3	41.4	8.3	9.6	24.5	42.6	65.7	100	1347	11	184	417	2	4.7	90.5	*	75.0	80.4	96.3
1/4	38.9	5.6	9.8	13.8	42.0	64.6	99.9	1080	*	224	493	2	4.7	87.5	*	82.5	83.4	91.3

* Incomplete analysis

TABLE 6- ANALYSIS OF LIGNITE AFTER ION EXCHANGE AND COMPOSITION OF EFFLUENT SOLUTION FOR VARYING ACID CONCENTRATION

Particle Size Range = -10 x +48 mesh
Solid/Liquid Mass Ratio = 1/2
Residence Time = 20.44 minutes

H_2SO_4 Concentration Normality x 100	Percent		Percent Cation Remaining In Lignite After Ion Exchange (MAF)					Effluent Concentration In ppm and pH						Material Balance, Percent				
	Moisture	Ash (MF)	Na	K	Mg	Ca	Al	Na	K	Mg	Ca	Al	pH	Na	K	Mg	Ca	Al
0**	39.0	10.4	76.0	44.5	100	99.8	100.0	634	*	5	12	0	6.6	99.8	*	96.0	99.7	94.4
4.131	39.5	9.9	28.3	46.5	94.6	99.2	100	1235	9	21	47	0	6.5	90.5	75.0	96.5	100.1	81.8
23.734	40.3	8.9	8.2	20.9	59.1	64.0	100	2150	23	340	609	0	5.5	95.1	36.3	89.4	95.4	98.9
46.51	38.5	6.3	6.0	9.3	47.6	53.6	81.7	1962	25	600	633	128	2.1	84.5	35.2	79.5	93.0	86.1
80.92	38.1	4.7	3.2	23.3	3.4	23.2	57.7	2553	34	578	700	274	1.7	96.4	57.6	107.0	94.4	91.6

**Distilled Water
* Incomplete Analysis

TABLE 7- ANALYSIS OF LIGNITE AFTER ION EXCHANGE AND COMPOSITION OF EFFLUENT FOR VARYING PARTICLE SIZE

Concentration of Input H_2SO_4 = 0.1118 N.
Residence Time = 20.44 minutes
Solid/Liquid Mass Ratio = 1/2

Particle Size, Mesh	Percent		Percent Cation Remaining In Lignite After Ion Exchange (MAF)					Effluent Concentration In ppm and pH						Material Balance, Percent				
Range	Moisture	Ash (MF)	Na	K	Mg	Ca	Al	Na	K	Mg	Ca	Al	pH	Na	K	Mg	Ca	Al
-10 x +14	35.2	5.2	9.3	11.1	57.5	73.9	100	257	*	148	712	3	4.5	93.2	*	65.7	90.7	68.8
-14 x +20	36.6	4.6	8.3	8.2	54.7	66.1	100	608	10	250	733	7	4.5	103.2	53.6	116.1	84.4	113.2
-20 x +28	36.2	4.6	2.8	8.5	45.3	40.1	99.1	1389	14	200	469	3	5.7	54.4	23.1	102.7	65.3	83.3
-28 x +35	40.0	5.5	5.0	11.0	35.8	61.9	99.9	1800	*	690	1270	2	6.3	88.3	*	93.6	91.9	79.0
-35 x +48	49.0	6.0	5.3	11.9	27.5	57.7	99.8	1922	*	760	1580	4	**	87.5	*	90.3	93.3	90.5

** Not Measured
* Incomplete Analysis

lignite per mass of MAF lignite to the mass of cation in original lignite per mass of MAF lignite. Material balances for each ionic species around the ion exchange unit was made for a steady state operation. The material balances for potassium were generally poor. This is due to very low concentration of potassium present in the original lignite. This leads to low levels of potassium which are very close to the detection limits on the atomic absorption unit, in the processed lignite and the effluent. The measurements for potassium are thus affected by the scatter of the machine.

Sample calculations are shown in Appendix C for calculating percent cations remaining in the lignite and the material balance closures from the data in Tables A-1 to A-4.

The ease of removal of the various cations from the lignite for all runs were found to be: $Na^{+} > K^{+} > Mg^{++} > Ca^{++} > Al^{+++}$. This is to be expected since the diffusion of ions from the lignite depends on the size and valence of the species among other factors as mentioned previously (20,24). The mobilities of species in ion exchangers normally decrease with increasing size and valence. The retardation of movement through pores and capillaries is also stronger for polyvalent than for monovalent ions.

Ash content of the processed lignite decreased for all runs from an average value of 11.4 percent (dry basis) in the original lignite to as low as 4.7 percent (dry basis), a decrease of 41 percent. The moisture content of the processed lignite from the ion exchange unit was approximately 50 percent. This was reduced to 40 percent by dewatering the product on Buchner funnel.

B. SOLID RESIDENCE TIME

The influence of solid residence time on the removal of sodium and other cations from lignite is shown in Figure 2. It can be seen from this figure that sodium is the easiest cation to exchange. The sodium content of the lignite decreased rapidly as residence time was increased from 10.22 to 51.1 minutes. For times greater than 5 minutes, no further reduction in sodium content was achieved. This would indicate that the sodium content approached equilibrium values. Similar results were obtained for potassium removal.

Significant reductions in magnesium and calcium content occurred for residence times greater than 3 minutes. This implies that once the monovalent cations content in the lignite reaches equilibrium values, then the divalent ions start to exchange with H^+ at a faster rate. The concentration of divalent cations in the lignite will also reach equilibrium given sufficient time. No appreciable reduction in aluminum was obtained for residence times less than ten minutes. Aluminum exists in lignite mainly as alumino-silicates, an inorganic mineral which is difficult to ion exchange (2).

The composition of various ions in the effluent is plotted as a function of solid residence time in Figure 3. The total cation concentration (iron-free) is plotted against residence time in Figure 4. As can be seen from Figure 3, the cation concentrations increased with time reaching maximum values at ten minutes residence time. The contribution of sodium to the total cation concentration in Figure 4 decreased with time while those of magnesium and calcium increased. The time needed to reach equilibrium during ion exchange by sodium is shorter than that needed by magnesium or calcium and

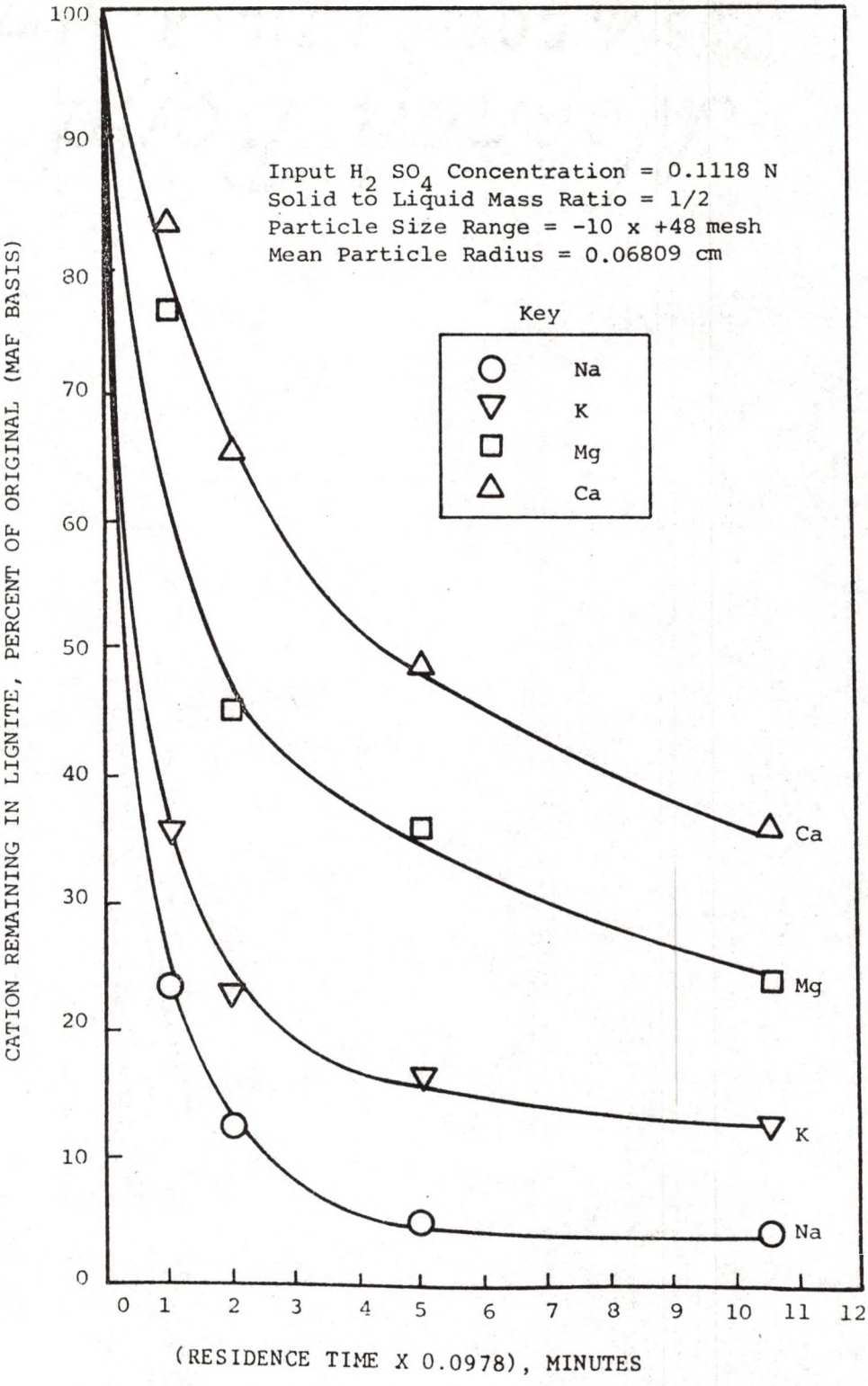

FIGURE 2 - CATION REMAINING IN LIGNITE AS A FUNCTION OF RESIDENCE TIME

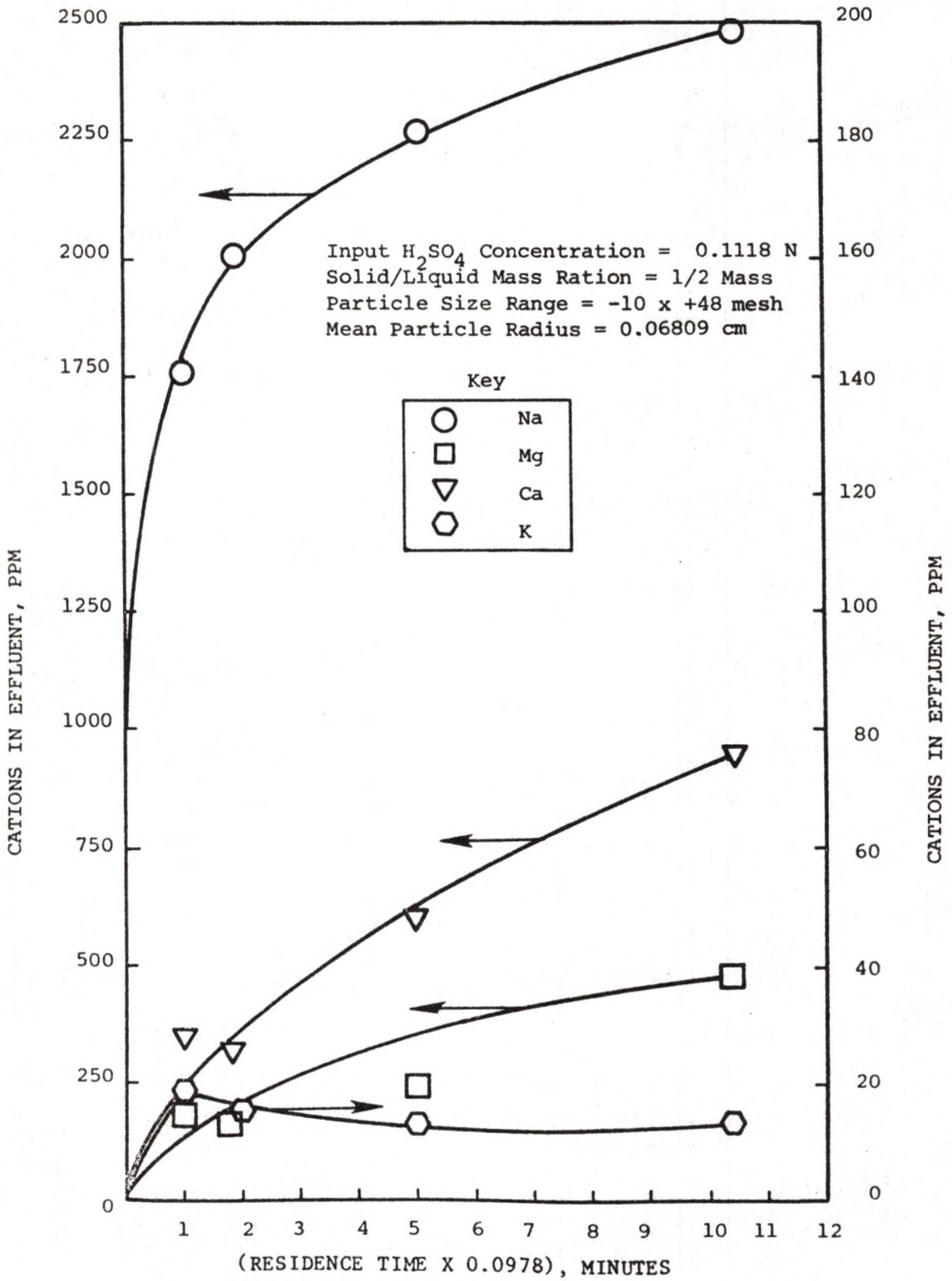

FIGURE 3 - CATION CONCENTRATION IN EFFLUENT AS A FUNCTION OF RESIDENCE TIME

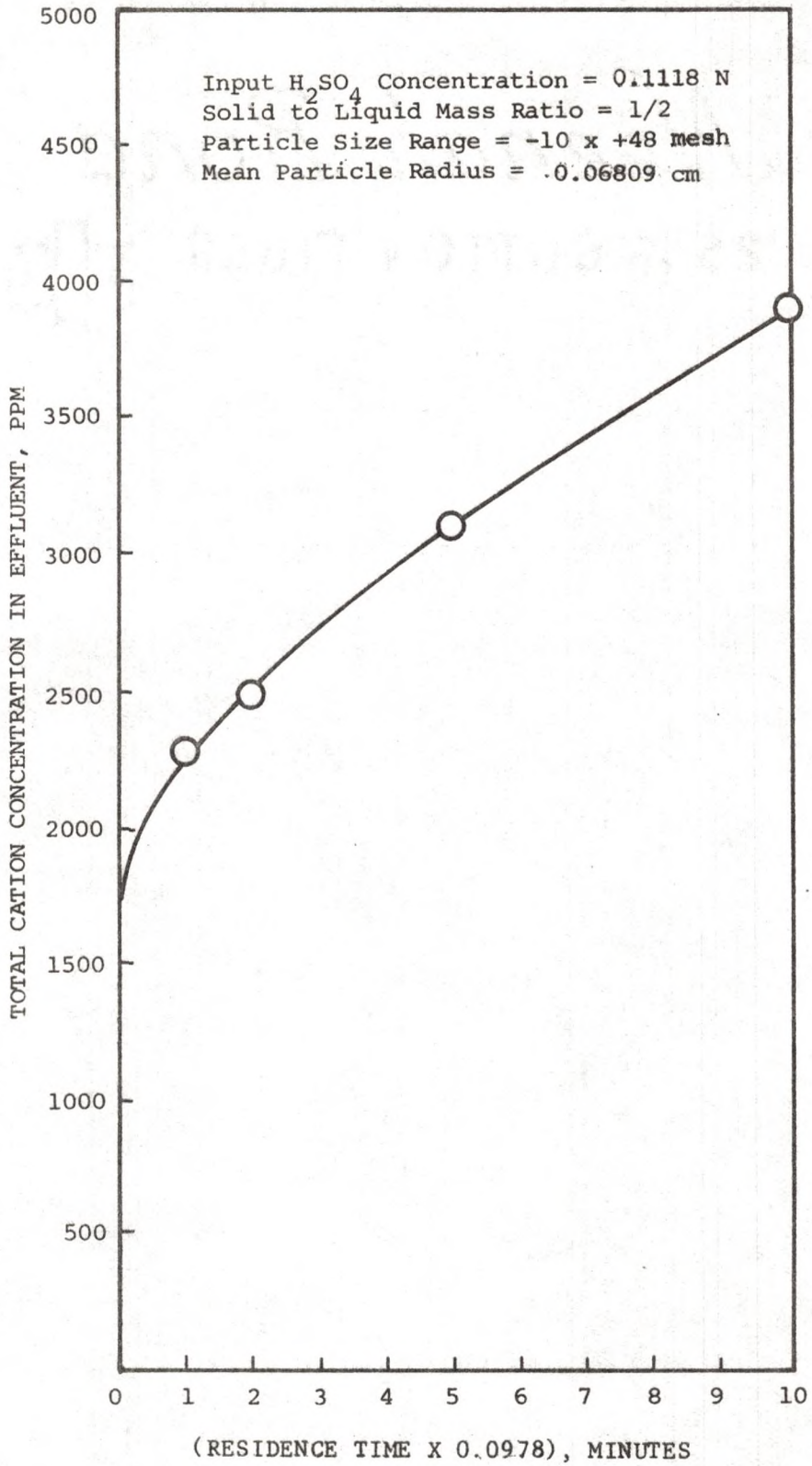

FIGURE 4 - TOTAL CATION CONCENTRATION AS A FUNCTION OF RESIDENCE TIME

hence, the fraction of sodium in the effluent will decrease with residence time while that of either magnesium or calcium increases.

Potassium made up less than a percent of the total cation concentration for all runs. The presence of aluminum was not detected in the effluents until 51.1 minutes residence time.

The material balance percent closures from 100 for Na^{+}, K^{+}, Mg^{++}, Ca^{++}, and Al^{+++} on the average were 9, 60, 17, 22, 11, respectively. Except for K^{+} and Ca^{++}, the rest showed good experimental accuracies.

C. SOLID/LIQUID MASS RATIO

The effect of decreasing the solid/liquid mass ratio was to increase the availability of H^{+} for exchange. Figure 5 is a plot of percent removal of the various ions as a function of solid/liquid mass ratio. Decreasing the solid/liquid mass ratio from 1/1 to 1/3 has a slight effect on increasing the sodium removal. Further decrease in the solid/liquid ratio does not achieve any further reduction in sodium content. The reduction in potassium follows a similar pattern.

The magnesium and calcium content of the lignite decreased very slightly with solid/liquid mass ratio decreasing from 1/1 to 1/4. The relative decrease was about five percent. The removal of aluminum in the range of solid/liquid mass ratios studied was less than one percent.

These observations qualitatively lead to the conclusion that solid/liquid mass ratio may not be a factor for values less than 1/2.

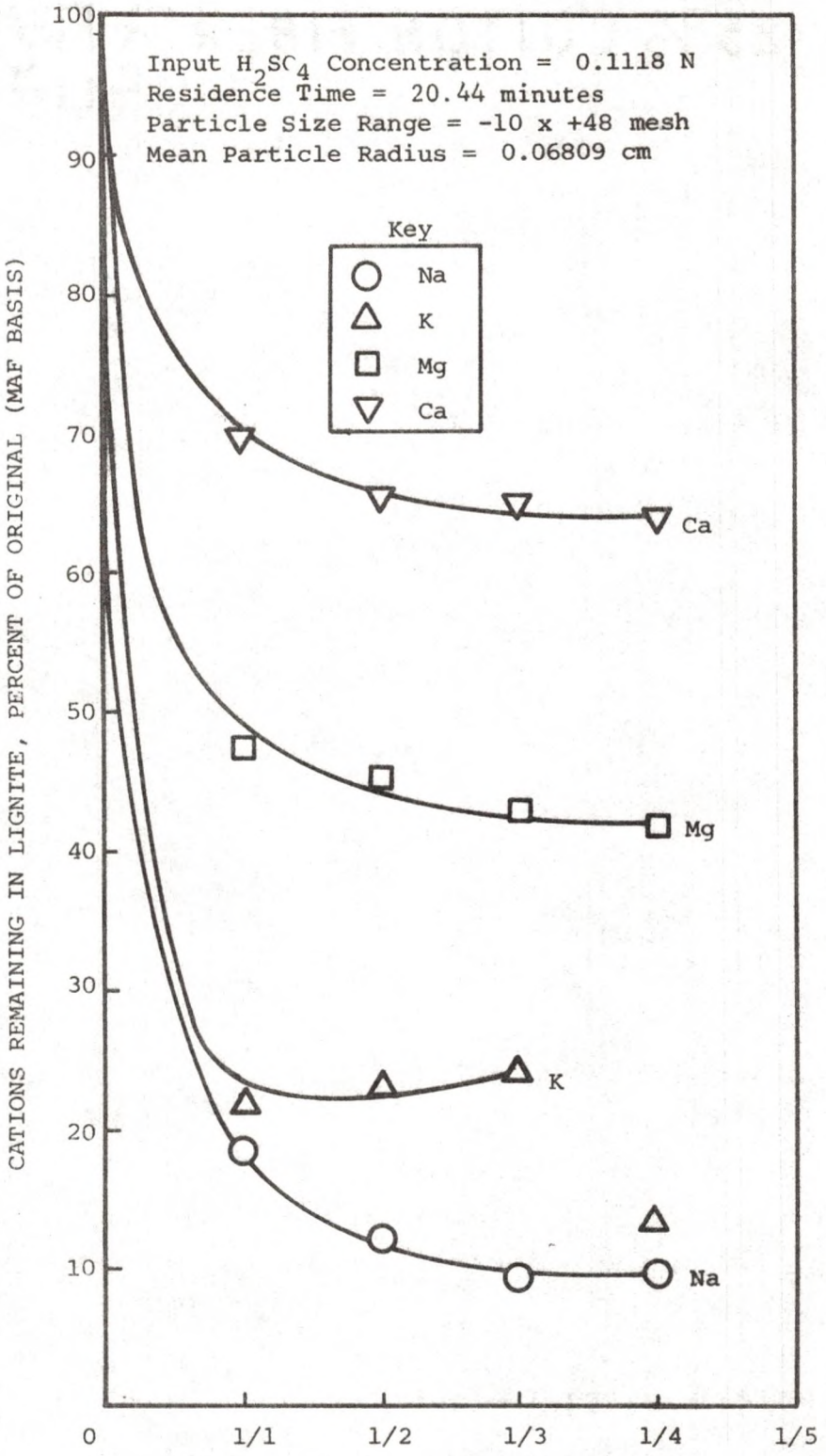

FIGURE 5 - CATION REMAINING IN LIGNITE AS A FUNCTION OF SOLID TO LIQUID MASS RATIO

The concentrations of the cations in the effluent are plotted as a function of solid/liquid mass ratio in Figure 6. The concentration of Na^+ in solution reached a maximum value when solid/liquid ratio was decreased to 1/2. This agrees with the fact that approximately the same amount of sodium is present in larger quantities of solution as solid/liquid mass ratio decreased from 1/1 to 1/4. Potassium in the solution reached a maximum concentration for 1/1 and then decreased. There was no detectable amount of Al^{+++} in any of the effluents.

The concentration of Mg^{++} and Ca^{++} in the effluent increased as solid/liquid mass ratio decreased. This is consistent with the fact that increased amounts of calcium and magnesium are removed at decreased solid/liquid ratios.

The total iron-free cation concentration as a function of solid/liquid mass ratio is given as Figure 7. When one compares Figures 6 and 7, the contribution of Na^+ to the total concentration is clearly seen. The fraction of Mg^{++} and Ca^{++} in the total cation concentration increased as solid/liquid mass ratio increased. Potassium was a minor contributor to total concentration for all runs.

The percent closures for the material balances of sodium, potassium, magnesium, calcium and aluminum were obtained as 18, 50, 18, 14, and 6, respectively.

D. SULFURIC ACID CONCENTRATION

To investigate the influence of H_2SO_4 concentrations on sodium removal runs were made with solutions varying from deionized

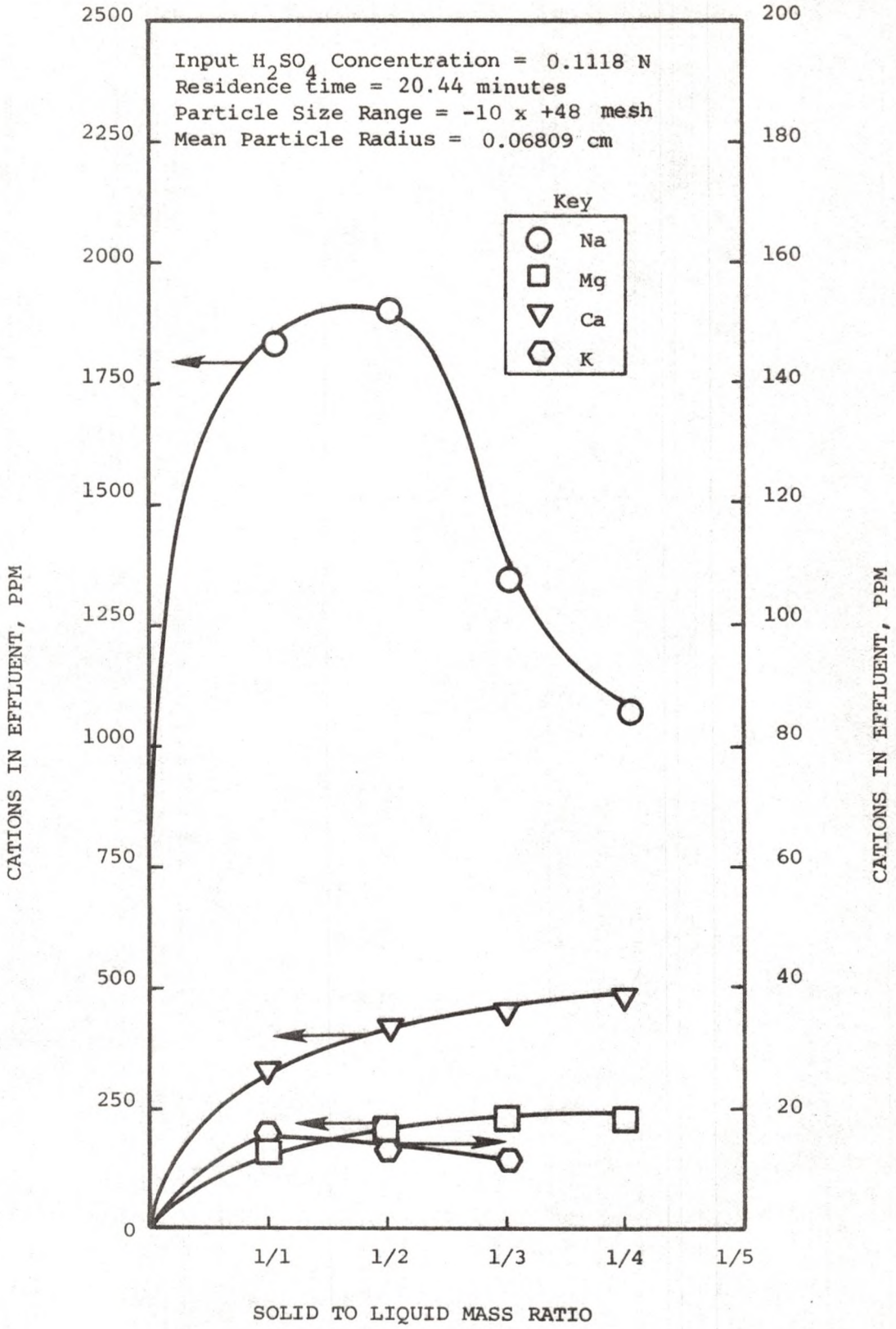

FIGURE 6 - CATION CONCENTRATION IN EFFLUENCT AS A FUNCTION OF SOLID TO LIQUID MASS RATIO

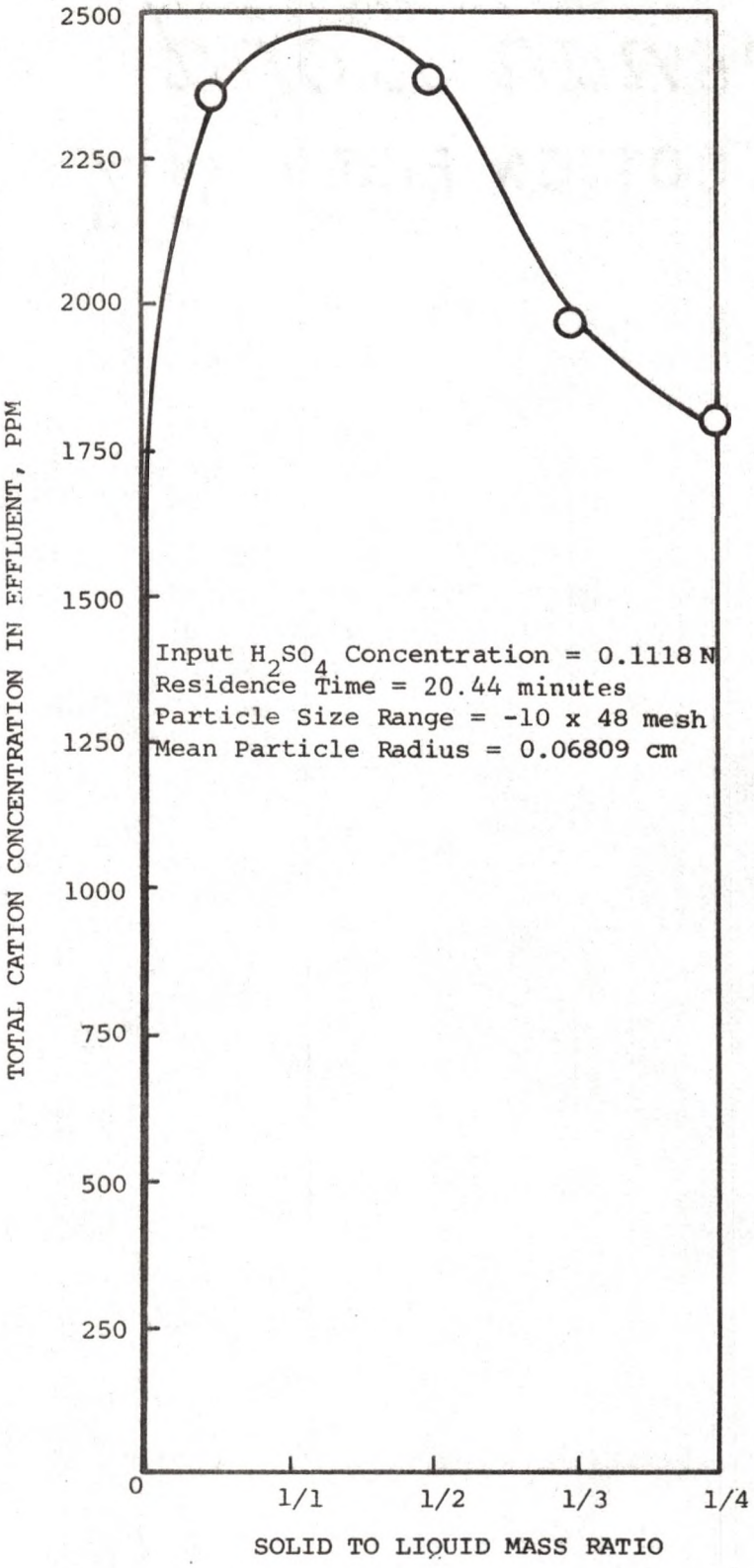

FIGURE 7 - TOTAL CATION CONCENTRATION IN EFFLUENT AS A FUNCTION OF SOLID TO LIQUID MASS RATIO

distilled water to 0.8092 N H_2SO_4 solution. Figure 8 is a graph of the percent removal of various ions plotted as a function of input solution concentration. Distilled water produced a 24 percent reduction for Na^+ and no reduction for Mg^{++}, Ca^{++} and Al^{+++}. A 55.5 percent reduction in K^+, which was more than twice the value for Na^+, was observed. This particular result seems to be in error. All other data indicated a higher reduction for Na^+ than for K^+ under similar experimental conditions.

The small percentage reduction of sodium using distilled water implies that distilled water is not an effective ion exchange medium since it lacks any significant amount of free exchangeable ions. A prolonged contact between distilled water and lignite and a large liquid/lignite ratio may eventually produce a marked reduction in sodium under a fixed bed system.

A progressive removal of the cations from lignite with increase in acid concentration was observed. The amount of sodium and potassium removed increased as the H_2SO_4 concentration increased reaching a limiting value for 0.4651 N H_2SO_4. The removal of magnesium and calcium progressed rapidly once the limiting values for sodium and potassium were reached.

No reduction in the aluminum content of lignite was observed until a concentration of 0.4651 N was used. Further increase in acid concentration showed a marked increase in the removal of aluminum from lignite. These results verify the fact that monovalents are exchanged first, followed by the divalents and trivalents.

The concentration of the cations in the effluent solution are plotted as functions of acid concentration in Figure 9. The

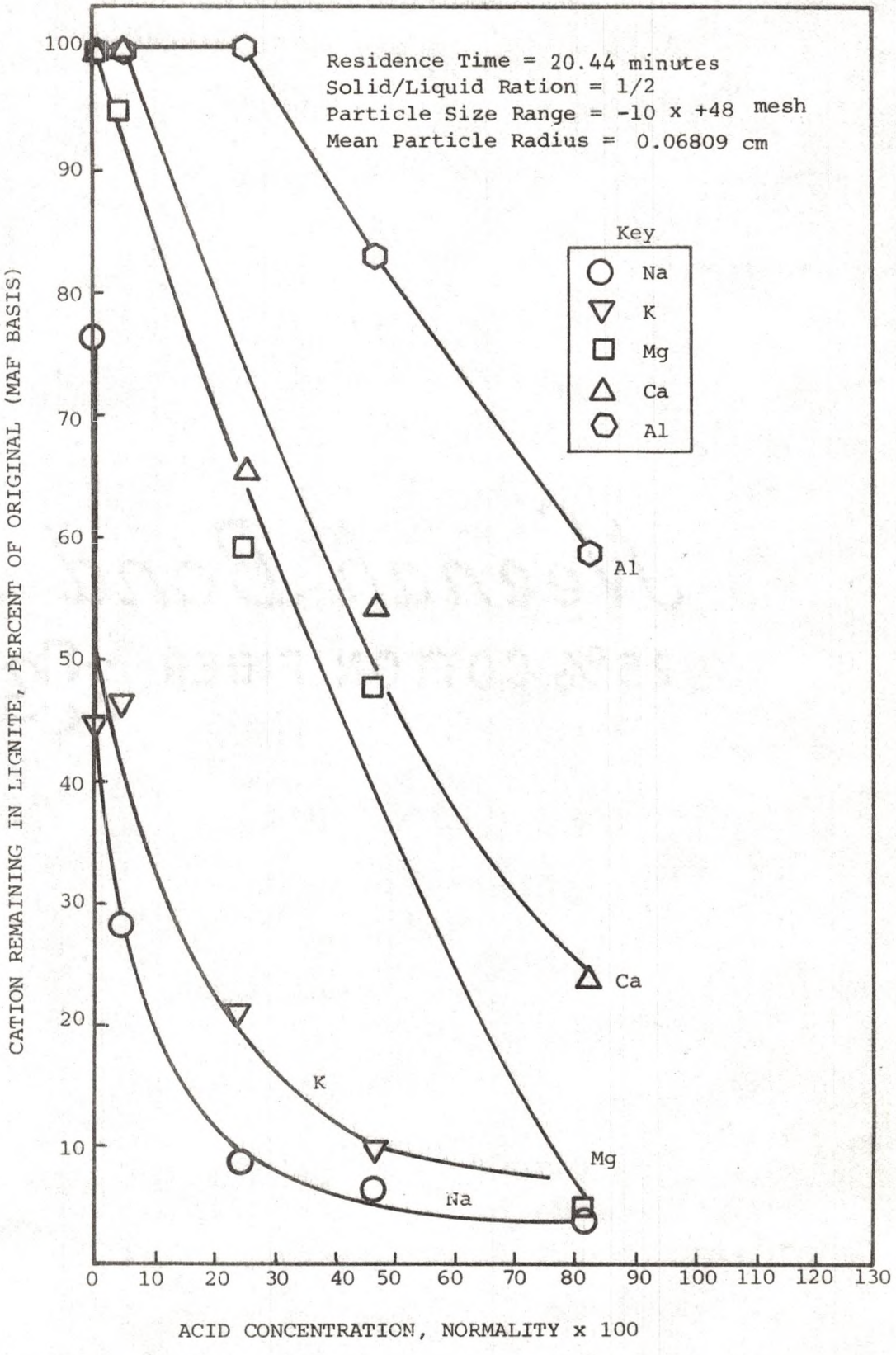

FIGURE 8 - CATION REMAINING IN LIGNITE AS A FUNCTION OF H_2SO_4 CONCENTRATION

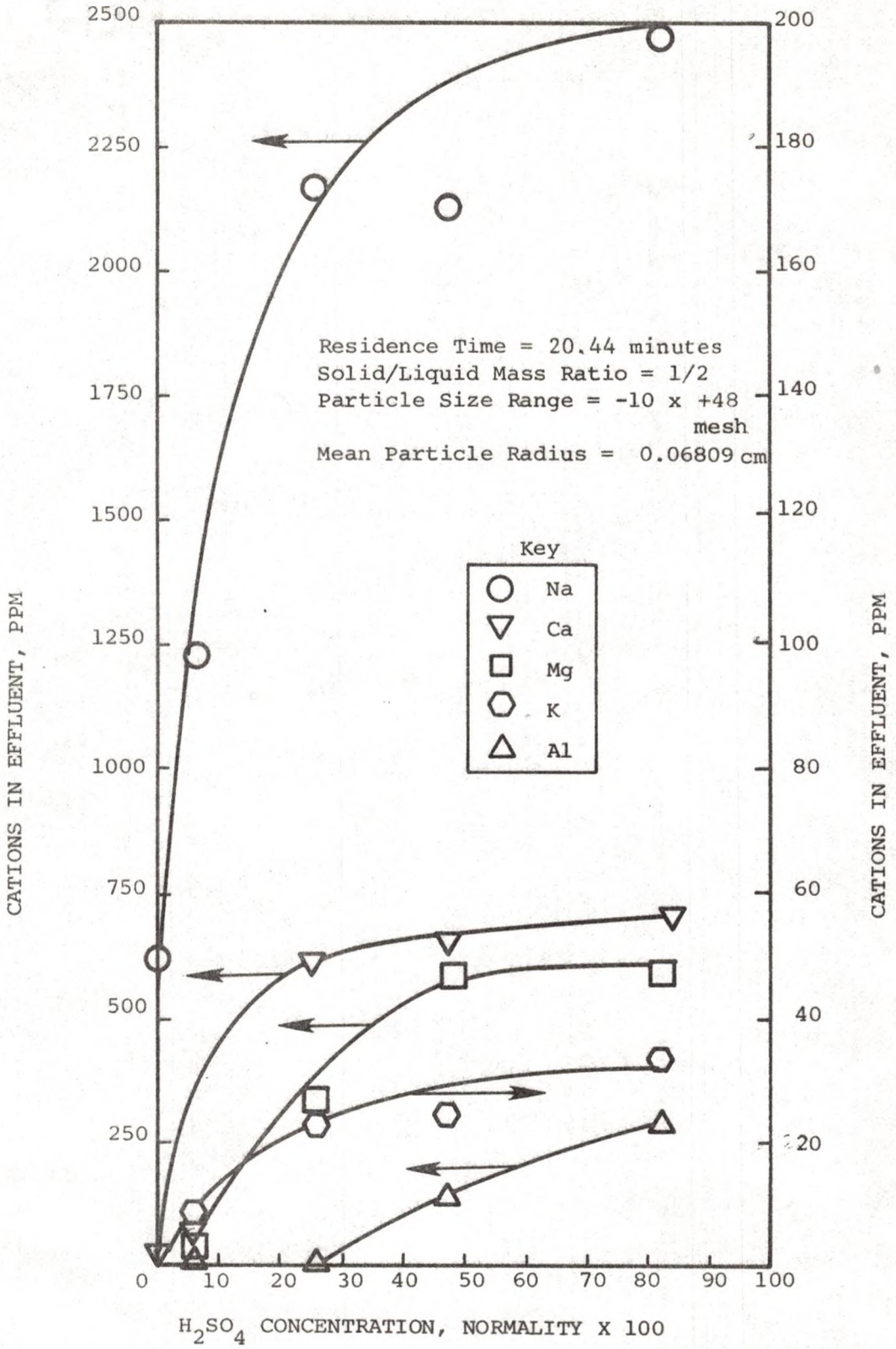

FIGURE 9 - CATION CONCENTRATION IN EFFLUENT AS A FUNCTION OF H_2SO_4 CONCENTRATION

concentrations of all the ions in the effluent increased with increase in solution concentration reaching maximum values at acid concentration of 0.8092 N. These observations are consistent with the fact that the removal of the cations from the lignite increases with the strength of the treating solution.

Figure 10 shows the total iron-free cation concentration in the effluent against solution concentration. The fraction of sodium in the effluent was highest for the distilled water run but decreased gradually as acid concentration increased while the contribution of Mg^{++} and Ca^{++} concentration increased. The amount of K^{+} present in any effluent was negligible. The percentage of Al^{+++} even for the two most concentrated runs was comparatively low. Since sodium is the easiest to replace, relatively low concentrations are effective in removing it from lignite but high concentrations will be required to replace magnesium and calcium. This fact is confirmed by the results obtained.

The material balance closures for this series of runs are the best as can be seen from the average percent closures from 100 for the ions involved, except for K^{+}: Na^{+} - 6.7, K^{+} - 49, Mg^{++} - 9, Ca^{++} - 3.5, Al^{+++} - 9.4.

E. PARTICLE SIZE

To determine the effect of particle size on ion exchange, lignite screened into -10 mesh x +14 mesh, -14 mesh x +20 mesh, -20 mesh x +28 mesh, - 28 mesh x +35 mesh and -35 mesh x +48 mesh (Tyler Standard Screen) was used. The percent removal of the various ions is plotted as a function of mean particle size in Figure 11.

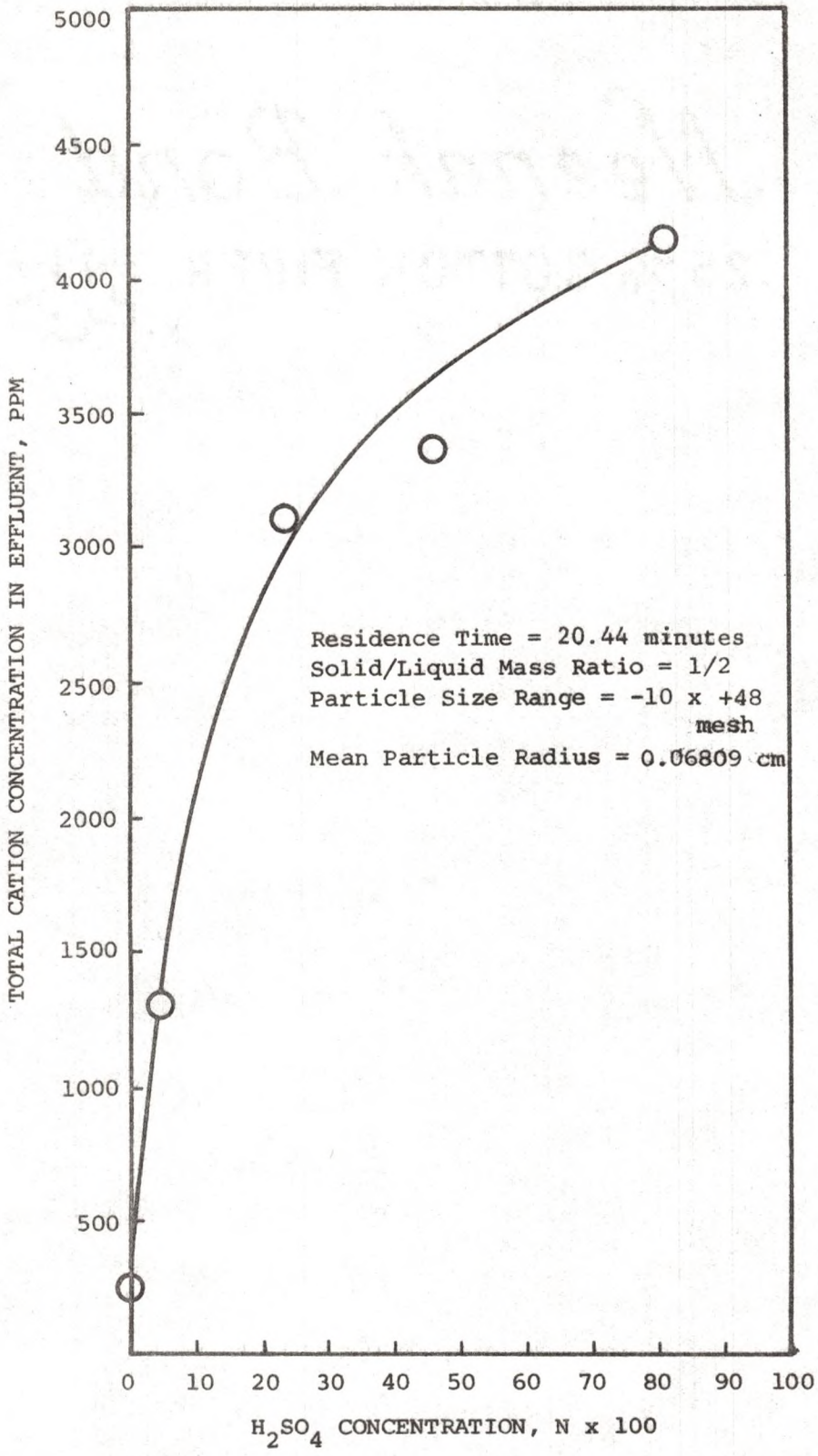

FIGURE 10 - TOTAL CATION CONCENTRATION IN EFFLUENT AS A FUNCTION OF H_2SO_4 CONCENTRATION

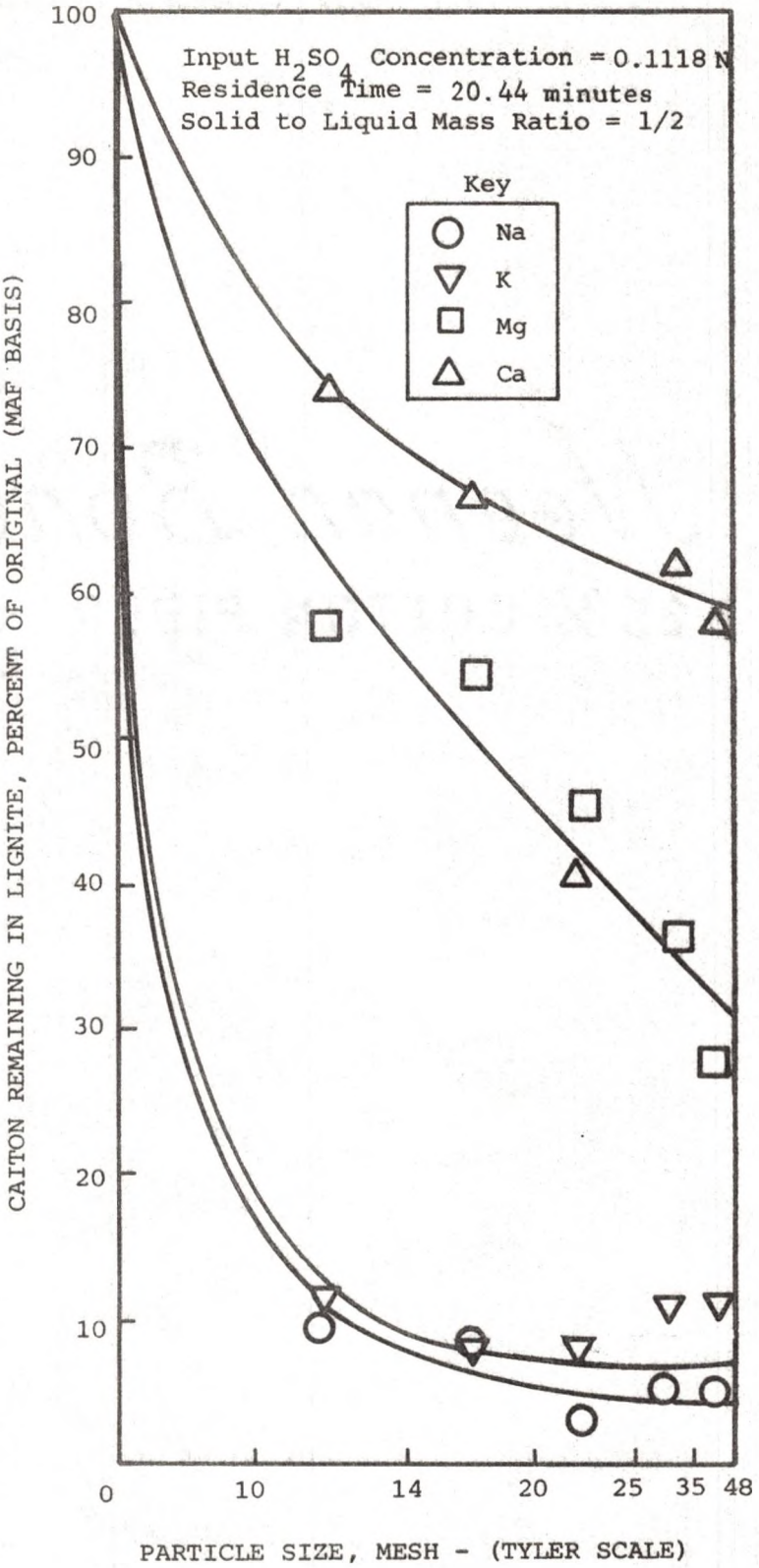

FIGURE 11 - CATION REMAINING IN LIGNITE AS A FUNCTION OF PARTICLE SIZE

The removal of sodium and other cations increases with decrease in particle size. For all particle sizes considered, a 90 percent or better reduction of sodium and potassium in the lignite was observed. For the range of -20 mesh x +28 mesh, the sodium left in the lignite was observed to be below the values obtained for -28 mesh x +35 mesh and for -35 mesh x +48 mesh. This is likely to be in error since it is the reverse of what it should be.

Significant reductions in magnesium content of the lignite occurred for the ranges of -20 mesh x +48 mesh. The removal of calcium from the lignite for the -20 mesh x +28 mesh was higher than the removal observed for -28 mesh x +35 mesh and -35 mesh x +48 mesh, another result that is definitely in error. The maximum reduction in calcium content was less than 40 percent. There was no reduction in the aluminum content of the lignite.

The results of particle size runs point out the fact that as particle size increases, the length of the capillaries that lead to the interior of the lignite particle will also increase increasing the diffusion path and tending to decrease the amount of ion removed in a given time. Thus, the use of larger particles for ion exchange will definitely require longer residence time to achieve the same degree of cation reduction in smaller sizes under identical experimental conditions.

Figure 12 is a plot of the effluent concentrations of the various ions as a function of the particle size. The concentrations of Na^{+}, Mg^{++} and Ca^{++} increased with decrease in particle size and

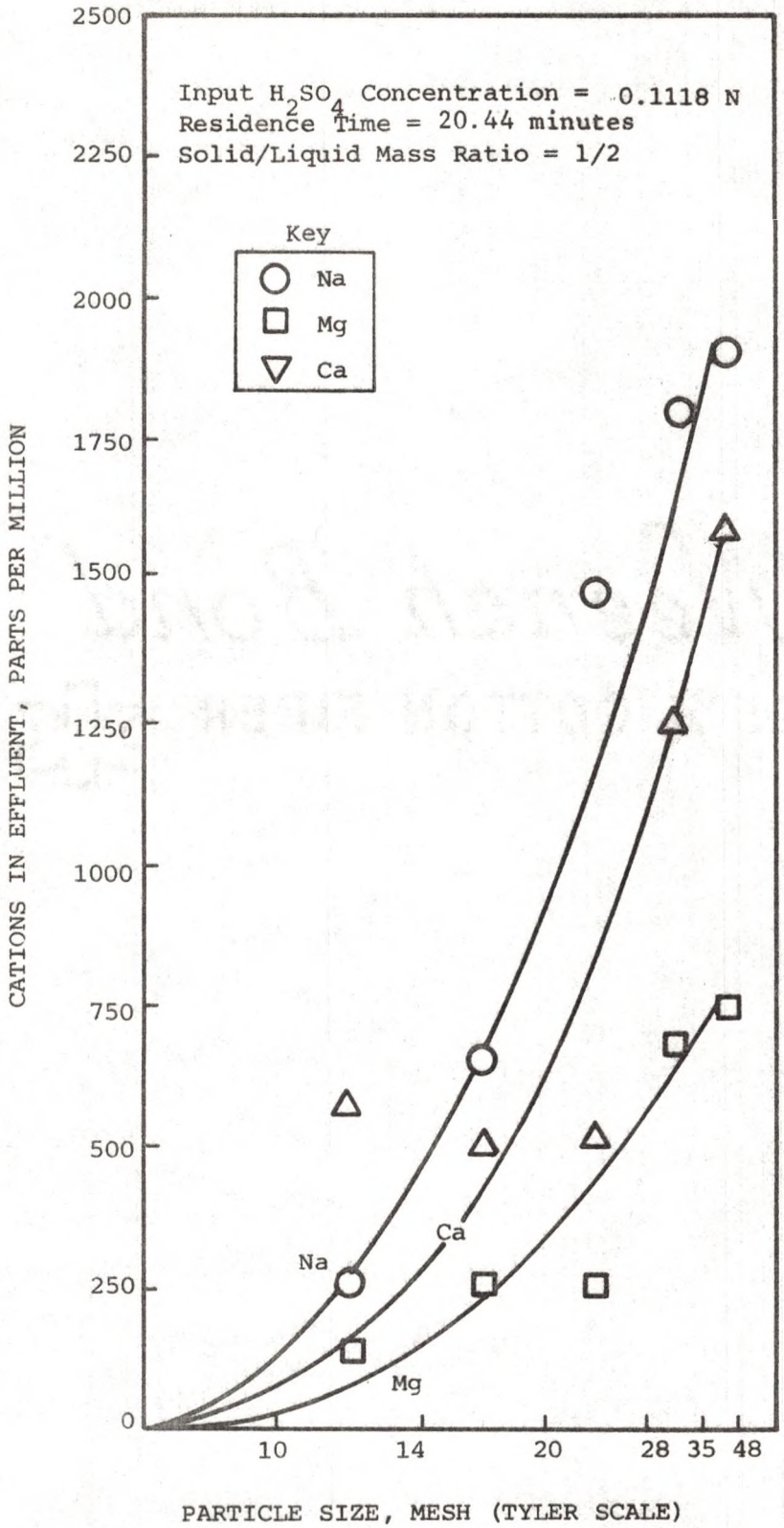

FIGURE 12 - CATIONS CONCENTRATIONS IN EFFLUENT AS A FUNCTION OF PARTICLE SIZE

reached maximum values for the smallest particle size used. This implies that the rate of removal of the cations from the lignite is much faster for smaller particle sizes as the distance of diffusion is shorter than for larger ones under the same given time. The total iron-free cation concentration is given in Figure 13 as a function of particle size. Sodium, calcium and magnesium, in that order, made the largest contributions to the total effluent concentration. Some effluents were not analyzed for K^+ and its contribution to total concentration was not determined. Aluminum in all effluents was quite negligible.

The percent material balance closures from 100 were 16 for Na^+, 14 for Mg^{++}, 15 for Ca^{++} and 18 for Al^{+++}. These were reasonably good reflections of the dependability of the experimental and analytical procedures within limits.

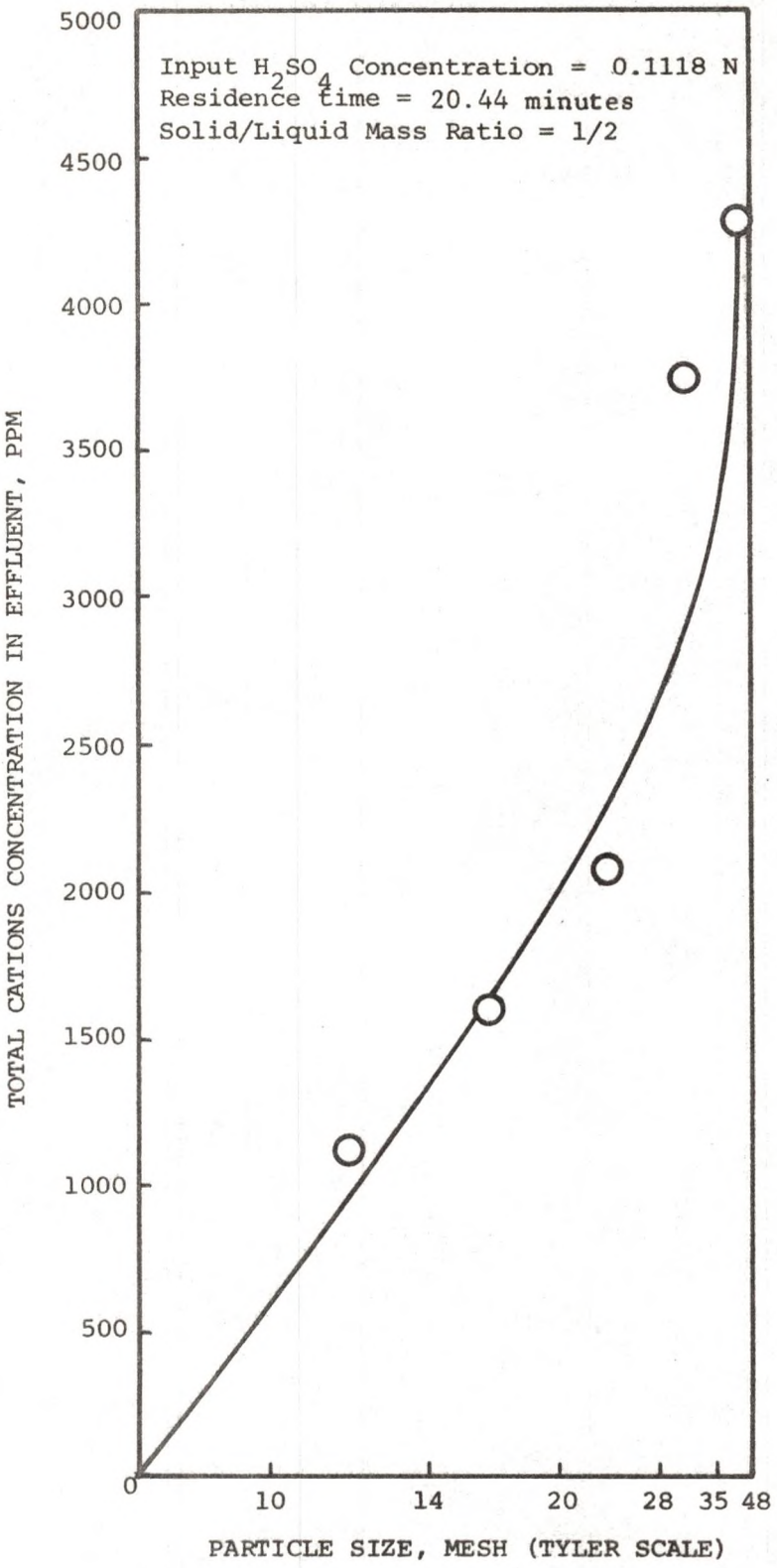

FIGURE 13 - TOTAL CATION CONCENTRATION IN EFFLUENT AS A FUNCTION OF PARTICLE SIZE

VII. THEORETICAL CORRELATION

A. GENERAL

Experimental results discussed in the previous section indicated that the removal of sodium and other cations from lignite by ion exchange is a function of the solid residence time, the initial solution concentration, the solid/liquid mass ratio and the particle size. These experimental conditions and the fact that the solutions used were dilute and the agitation was insufficient (20) favor film diffusion control over particle diffusion control as the rate controlling step as indicated by equations 11 and 12. Therefore, film diffusion is postulated to be the rate controlling step for the exchange of sodium from lignite by H^+ in the continuous countercurrent unit used. However, it is to be noted that a sharp limit between particle and film diffusion does not exist and both mechanisms may play important roles during the exchange process. In fact, Helfferich points out that every ion exchange is film-controlled during an initial period and the tendency towards particle diffusion control increases gradually (20). The residence times used, except for two runs, were 2 minutes and under and it is most likely that film diffusion would be the rate controlling step.

Equation 12 for film diffusion control was derived for infinite solution volume, complete conversion, counter ions of equal mobility, and no ion selectivity. None of these assumptions can be taken to be true for the exchange of Na^+ and H^+ in the countercurrent unit used.

The independent variables in equation 12 are t, c, $1/r_o$ and $1/\delta$. The film thickness δ is dependent on solid/liquid mass ratio.

The values of D and $\overline{C}$ were calculated, as shown in Appendix C and substituted in equation 12 to give equation 16 which was subsequently used to predict sodium remaining in the lignite after ion exchange.

$$F(t) = 1 - \exp(-1.964 \times 10^{-5}\ Ct/r_o\delta) \qquad (16)$$

B. LINEAR LEAST-SQUARES FIT

The least-squares fit determines the "best fit" of an assumed implicit linear or non-linear function to experimental data by minimizing the sum of squares of the deviations in the y direction of the data points (Xi, Yi) from the most probable curve (25). Based on the plots of the experimental results for the removal of sodium and from theory, an exponential function defined by equation 17 was postulated to give the best fit for the data.

$$Y = \exp(-k\ x^a_1\ x^b_2\ x^c_3\ x^d_4) \qquad (17)$$

where Y = percent sodium removed from lignite;

x_1 = t, seconds;

x_2 = solid/liquid ratio P, dimensionless;

x_3 = C, meq/cm^3;

x_4 = $1/r_o$, cm^{-1};

a, b, c, d, and k = constants.

Equation 18 defines another possible function that can be used to find the best fit for the data. It is based on an empirical regression fit.

$$Y = (m\ x^f_2\ x^g_3\ x^h_4)\ (\exp - x_1/e) \qquad (18)$$

where e, f, g, h, and m = constants.

A one and two-step logarithmic transformations were used to linearize equations 17 and 18. Data for a linear multiple linear regression

between the dependent and independent variables were generated from Tables 4 to 7.

Equations 17 and 18 with least-squares estimates of a, b, c, d, and k and of e, f, g, h, and m are given as equations 19 and 20, respectively.

$$Y = \exp\left(-0.160 \frac{t^{0.316} C^{0.259}}{p^{0.241} r_o^{0.274}}\right) \tag{19}$$

$$Y = 0.359 \left(\frac{C^{-0.574}}{p^{-0.461} r_o^{-0.673}}\right) (\exp 0.000236t) \tag{20}$$

Analysis of variance for the regression of equation 19 is given in Table 8. The multiple correlation coefficient (R^2) and the partial F statistic for each variable were based on a regression equation containing that variable and the variable initially entered. The multiple correlation coefficient for equation 20 was 0.845 about two percent less than that of equation 19 and hence equation 19 was chosen to be used subsequently.

The values of R^2_1, individual correlation coefficients, were obtained by entering each variable separately in the regression to find the heirarchy of the variables in predicting Y. As can be seen from Table 8, concentration and time are the two variables that explain most of the variation in Y. The values of R^2 increased with the increase in the number of variables used in the regression. This indicates the importance of each variable to the total prediction of Y.

A sample calculation for partial F is given in Appendix C. The total F statistic is greater than $F_{4, 11, 1-\alpha}$ ($\alpha = 0.10$) where α is the probability that a variable will exceed a certain

TABLE 8 - ANALYSIS OF VARIANCE (ANOVA) FOR REGRESSION ON EQUATION 19

Source		d.f.[a]	S.S.[b]	M.S.[c]	Partial F	Overall F	R^2	R^2_1
Regression	x_1	1	0.299	0.299	4.65	7.832	0.499	0.499
	x_2/x_1[d]	1	0.053	0.053	0.813		0.541	0.198
	$x_3/x_1, x_2$	1	0.441	0.441	13.0		0.813	0.561
	$x_4/x_1, x_2, x_3$	1	0.094	0.094	3.31		0.860	0.236
Residual		11	0.312	0.0284				
Total		15	1.199					

[a] degrees of freedom

[b] sum of squares

[c] mean square

[d] x_2 entered after x_1

value, showing the significance of the overall regression. However, from each partial F tests, tests that assess whether the addition of any specific independent variable, given others already in the model, significantly contributes to the overall correlation, the following conclusions can be reached at $\alpha = 0.10$: (a) x_1 and x_3 significantly add to the prediction of Y by the model; (b) x_4 is barely significant; and (c) x_2 does not contribute to the overall picture. Thus, a regression without x_2 was performed and the multiple correlation coefficient obtained 0.828 was 3.7 percent less than 0.860 of the full model. The values of a, c, d and k for the model without x_2 were 0.312, 0.256, 0.270 and 0.404, respectively. Despite the fact that x_2 did not add much to the overall correlation, it was incorporated in the regression equation 19 since solid/liquid ratio in the experimental runs has shown a significant effect on the rate of sodium removal up to 1/2.

C. PREDICTION

The percent sodium (MAF) remaining in lignite was estimated using equations 16 and 19. Each independent variable was varied one at a time. The results of these predictions along with experimental values are assembled in Tables 9 through 12. The percent of sodium remaining in lignite as a function of residence time, solid/liquid ratio, acid concentration and particle size is plotted in Figures 14 to 17. As can be seen from these tables and still more strikingly from the figures, there is a reasonably good agreement between the experimental and predicted values. This demonstrates the applicability of the theoretical and least-squares models in

TABLE 9 - EFFECT OF RESIDENCE TIME ON PERCENT SODIUM REMAINING IN LIGNITE AFTER ION EXCHANGE

Input H_2SO_4 Concentration = 0.1118 N
Solid/Liquid Mass Ratio = 1/2
Particle Size Range = -10 x +48 mesh
Mean Particle Radius = 0.06809 cm
Concentration of Fixed Ionic Sodium = 12.77 meq/cm^3
Diffusion Coefficient = 8.545 x 10^{-4} cm^2/sec

Residence Time, seconds	Percent Sodium Remaining		
	Experimental	Linear Least-Squares Fit (Equation 19)	Theoretical Model (Equation 16)
638	23.9	18.3	24.7
1226	12.4	12.3	9.1
3066	4.9	6.0	4.2
6408	4.1	2.9	4.1

TABLE 10 - EFFECT OF SOLID/LIQUID MASS RATIO ON PERCENT SODIUM REMAINING IN LIGNITE AFTER ION EXCHANGE

Input H_2SO_4 Concentration = 0.1118 N
Particle Size Range = -10 x +48 mesh
Mean Particle Radius = 0.06809 cm
Residence Time = 20.44 minutes
Concentration of Fixed Ionic Sodium = 12.77 meq/cm^3
Diffusion Coefficient = 8.545 x 10^{-4} cm^2/sec

Solid To Liquid Mass Ratio	Percent Sodium Remaining		
	Experimental	Linear Least-Squares Fit (Equation 19)	Theoretical Model (Equation 16)
1/1	18.7	14.8	14.7
1/2	12.4	12.3	14.4
1/3	9.6	9.1	13.9
1/4	9.7	8.5	13.9

TABLE 11 - EFFECT OF H_2SO_4 CONCENTRATION ON PERCENT SODIUM REMAINING IN LIGNITE AFTER ION EXCHANGE

Particle Size Range = -10 x +48 mesh
Mean Particle Radius = 0.06809 cm
Solid/Liquid Mass Ratio = 1/2
Residence Time = 20.44 minutes
Concentration of Fixed Ionic Sodium = 12.77 meq/cm^3
Diffusion Coefficient = 8.545 x 10^{-4} cm^2/sec

H_2SO_4 Concentration, N x 100	Percent Sodium Remaining		
	Experimental	Linear Least-Squares Fit (Equation 19)	Theoretical Model (Equation 16)
4.131	28.3	20.0	35.9
23.74	8.2	7.8	3.8
46.51	6.0	4.8	3.7
80.92	3.6	3.0	3.6

TABLE 12 - EFFECT OF PARTICLE SIZE ON PERCENT SODIUM REMAINING IN LIGNITE AFTER ION EXCHANGE

Input H_2SO_4 Concentration = 0.1118 N
Residence Time = 20.44 minutes
Solid/Liquid Mass Ratio = 1/2
Concentration of Fixed Ionic Sodium = 12.77 meq/cm^3
Diffusion Coefficient = 8.545 x 10^{-4} cm^2/sec

Particle Size, cm	Percent Sodium Remaining		
	Experimental	Linear Least-Squares Fit (Equation 19)	Theoretical Model (Equation 16)
0.1168	9.3	16.5	22.2
0.08407	8.3	13.8	13.9
0.05893	5.0	9.1	5.4
0.02946	5.3	7.1	5.3

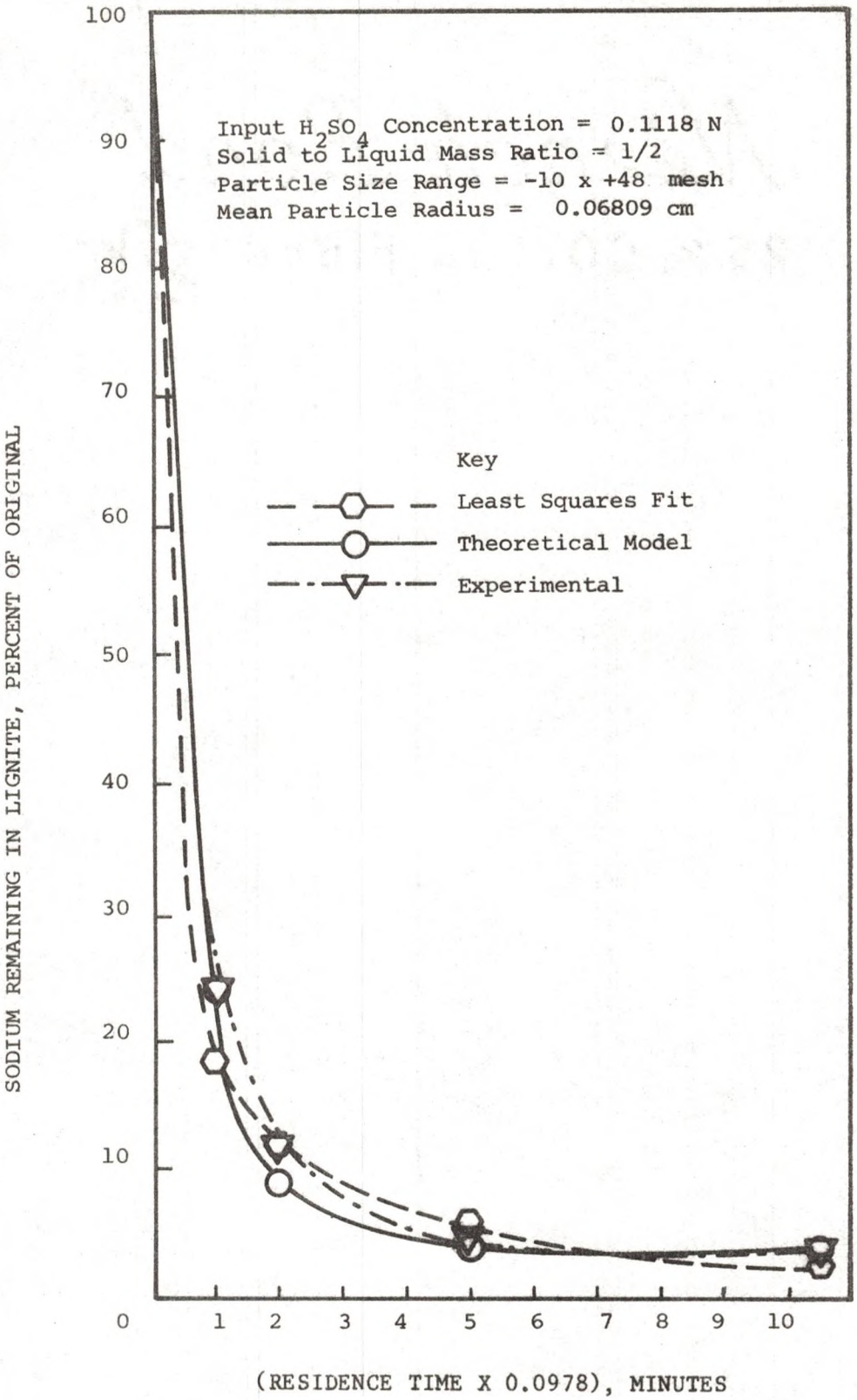

FIGURE 14 - SODIUM REMAINING IN LIGNITE AS A FUNCTION RESIDENCE TIME

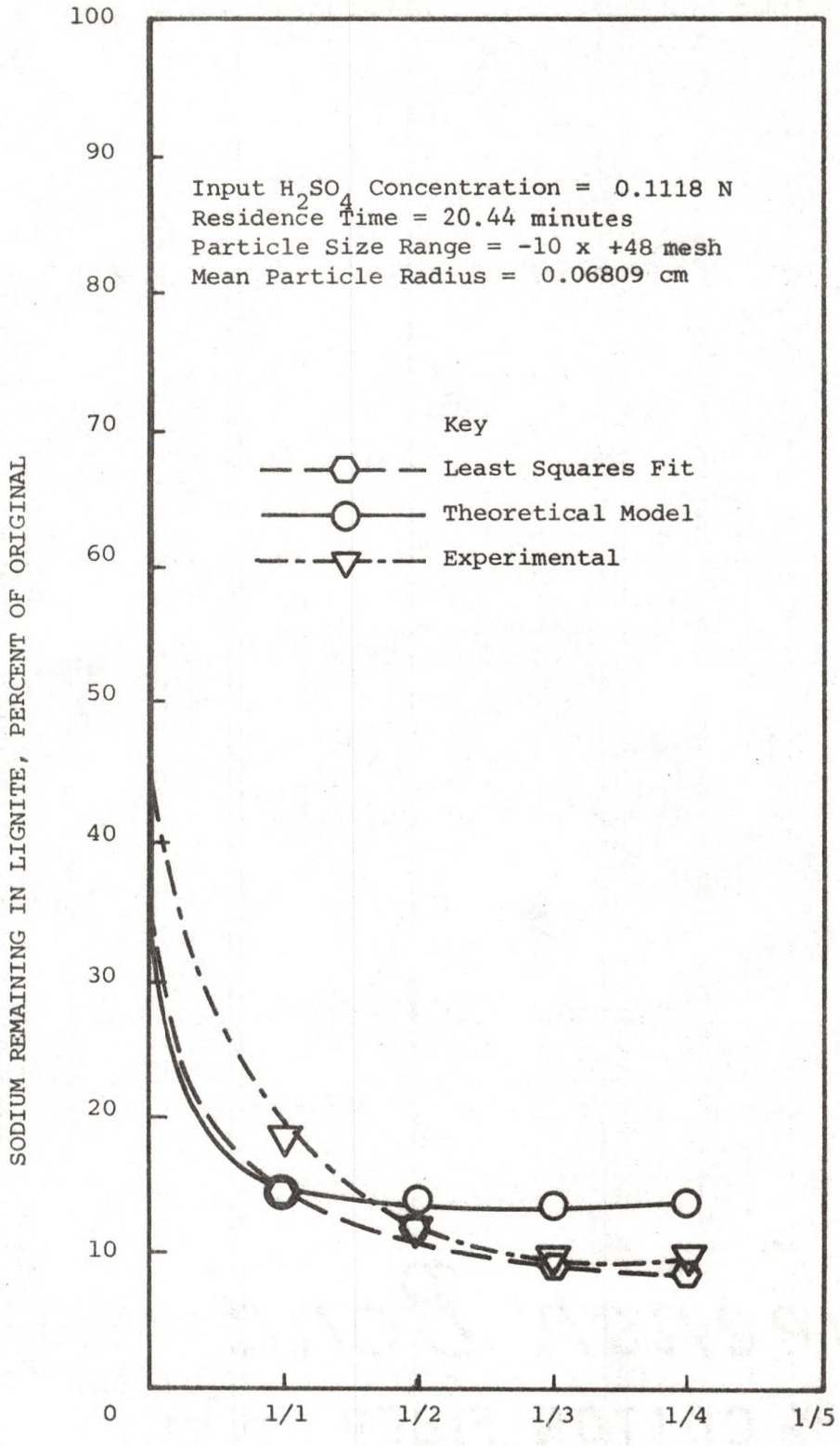

FIGURE 15 - SODIUM REMAINING IN LIGNITE AS A FUNCTION OF SOLID TO LIQUID MASS RATIO

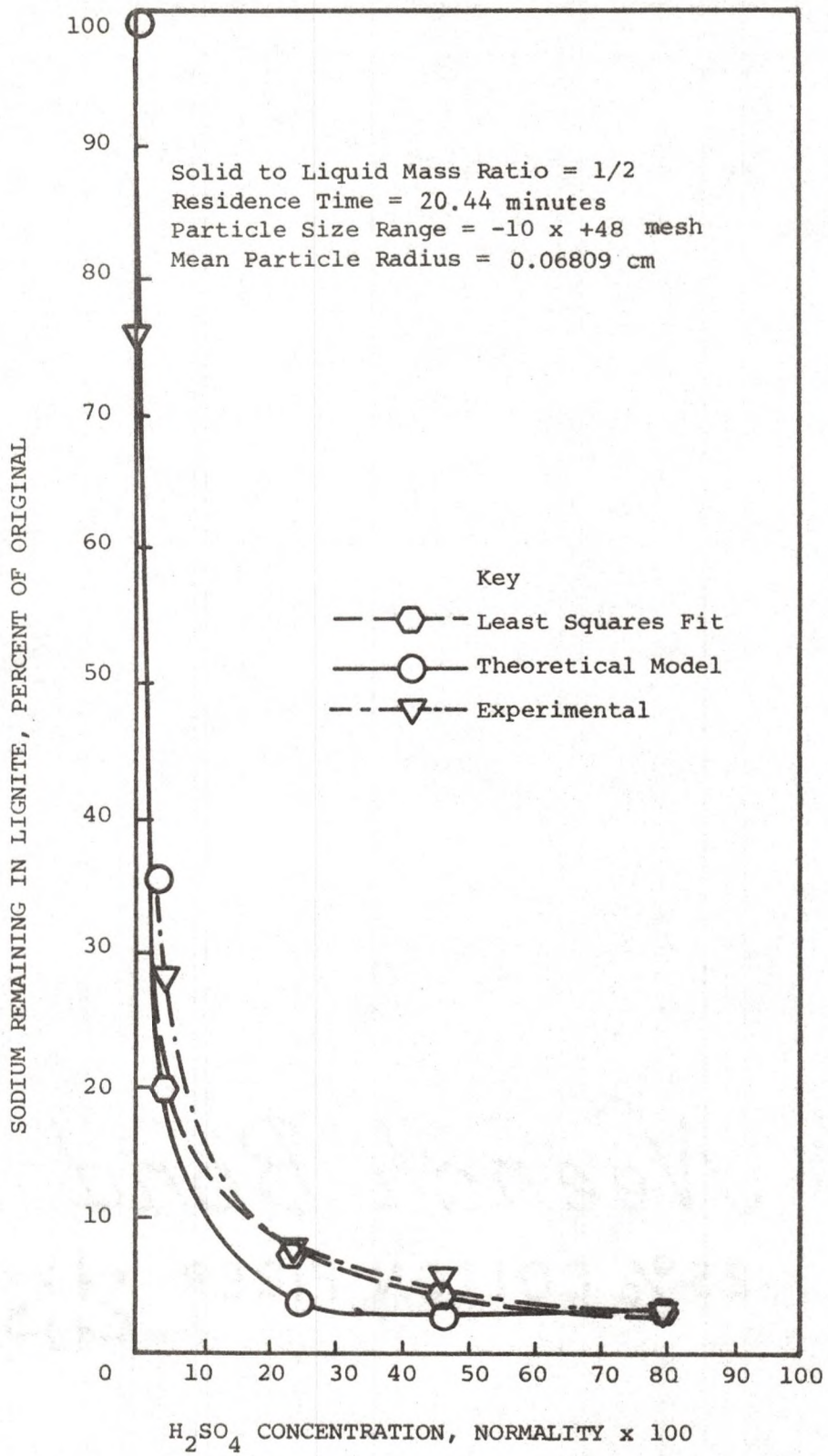

FIGURE 16 - SODIUM REMAINING IN LIGNITE AS A FUNCTION OF H_2SO_4 CONCENTRATION

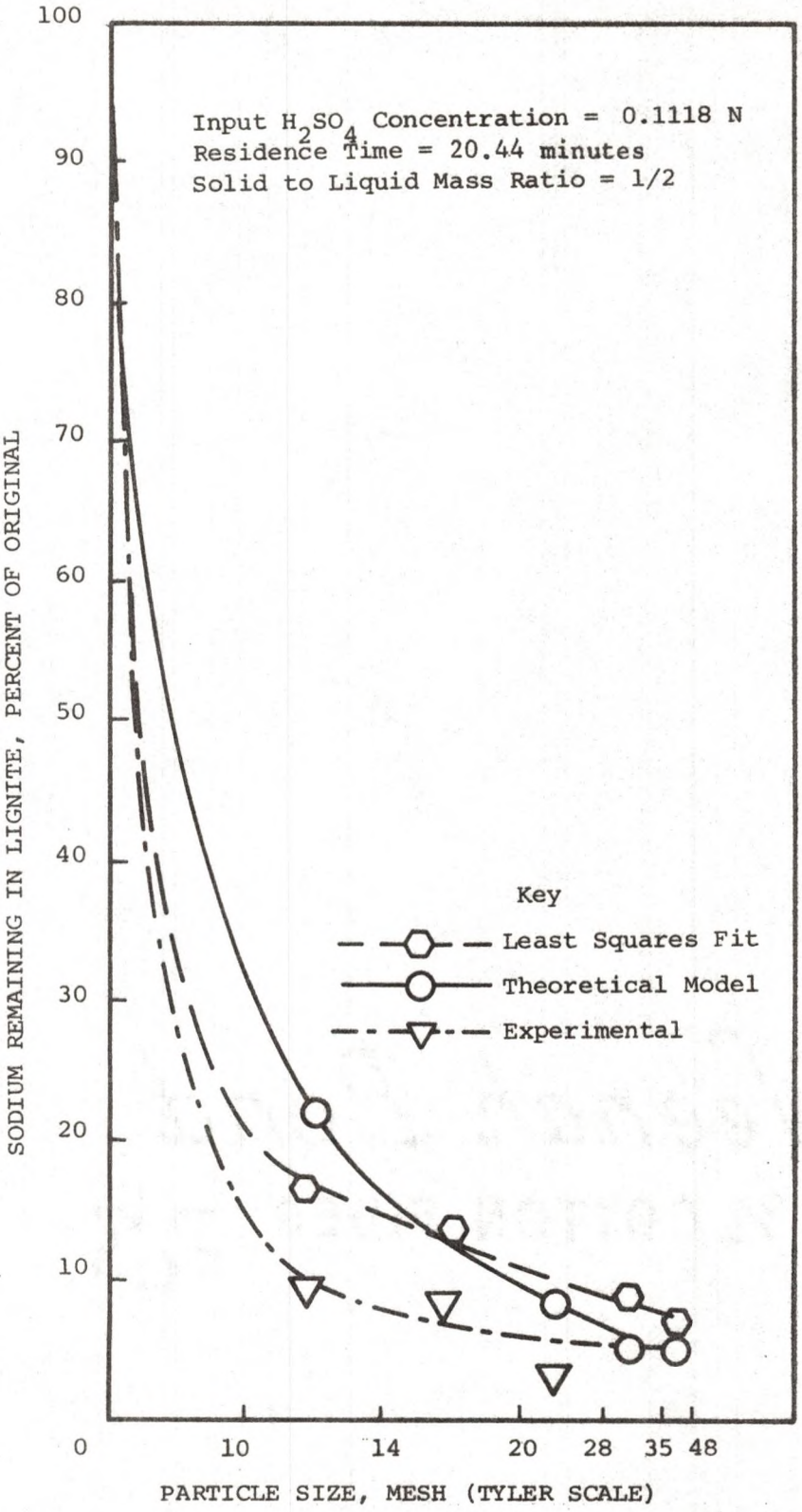

FIGURE 17 - SODIUM REMAINING IN LIGNITE AS A FUNCTION OF PARTICLE SIZE

design procedures. The deviations that did occur were probably the results of experimental errors or in the case of the theoretical model, the many simplifying assumptions involved.

The conclusions reached on the experimental results of sodium removal from lignite are supported by the theoretical model. The theoretical model showed its greatest deviation from experimental data for particle size runs. This is due to the lack or nonavailability of accurate methods of determining the exact particle sizes. The least-squares estimates for some runs are seen to vary more than the theoretical predictions from the experimental data. This probably is attributable to the two steps logarithmic transformation used to linearize the postulated exponential function.

VIII. CONCLUSIONS

From the experimental and theoretical correlation results the following conclusions are reached.

1. The rate of sodium and other cations removed from lignite by ion exchange increased with increase in residence time and acid concentration and with decrease in solid/liquid mass ratio and particle size.

2. Sodium is the easiest cation to replace followed by K^{+}, Mg^{++}, Ca^{++} and Al^{+++}.

3. Residence time of greater than 50 minutes did not achieve any further reduction in sodium content of the lignite.

4. Solid/liquid mass ratio less than 1/2 produced no significant increase in sodium removal.

5. Sulfuric acid concentration greater than 0.4651 was not needed to achieve an almost complete removal of sodium from lignite.

6. Particle sizes less than 35 mesh would be unnecessary to reduce the sodium content of the lignite to less than five percent.

7. The postulated film diffusion model for the removal of sodium agrees well with experimental results.

8. The postulated exponential function fit explains about 86 percent of the variation in the experimental data.

9. The heirarchy of the independent variables in contributing to an overall correlation of the dependent variable, percent sodium remaining in lignite, is found to be concentration, residence time, particle size and solid/liquid ratio.

IX. RECOMMENDATIONS

Some suggestions for future experimental work are given below.

1. The continuous countercurrent ion exchange unit used for the present work was not long enough to have sufficient variability in residence time. A modification of this unit would be warranted.

2. Use of different cations, such as Ca^{++}, Mg^{++}, Al^{+++}, Fe^{+++}, would be necessary to investigate and compare the efficiency of exchange ions in the removal of sodium from lignite.

3. Lignites of different sodium content should be used to find the dependence of sodium removal on the initial amount of sodium in the lignite.

4. The use of Latin square or other experimental designs would be helpful to reduce the number of runs needed to investigate the influence of the different parameters. Such a design would also help to reduce experimental errors and explain the interactions of the parameters.

5. The theoretical model and the linear least squares fit used for sodium removal should be tried for the removal of the other cations.

APPENDIX A

RAW EXPERIMENTAL DATA

TABLE A-1. - ANALYSIS OF LIGNITE AFTER ION EXCHANGE FOR VARYING RESIDENCE TIME

Input H_2SO_4 Concentration = 0.1118 N
Particle Size Range = -10 x +48 mesh
Solid/Liquid Mass Ratio = 1/2

Residence Time, Minutes	Ash % (MF)	Composition in MAF Coal, ppm					Composition In Ash, %				
		Na	K	Mg	Ca	Al	Na_2O	K_2O	MgO	CaO	Al_2O_3
0*	11.4	60.24	3.2	24.5	109	52.5	9.2	0.4	5.2	20.7	11.5
10.22	6.1	30	2.4	38.5	119	93	4.4	0.3	5.1	18.0	11.1
20.44	5.2	16	1.6	23.2	116	78	2.2	0.2	3.8	16.2	14.7
51.1	7.4	5	0.90	14.6	93	81	0.7	0.1	2.6	14.1	16.6
102.2	5.6	5.5	0.93	13.2	92	99	0.8	0.1	2.4	14.2	20.6

*As-Received Lignite

TABLE A-2. - ANALYSIS OF LIGNITE AFTER ION EXCHANGE FOR VARYING SOLID/LIQUID MASS RATIO

Input H_2SO_4 Concentration = 0.1118 N
Particle Size Range = -10 x +48 mesh
Residence Time = 20.44 minutes

Solid/Liquid Mass Ratio	Ash %	Composition In MAF Coal, ppm					Composition In Ash, %				
		Na	K	Mg	Ca	Al	Na_2O	K_2O	MgO	CaO	Al_2O_3
1/1	8.6	16	0.99	16.3	113	68.5	2.4	0.1	3.0	17.2	14.1
1/2	5.2	16	1.6	23.2	116	78	2.2	0.2	3.8	16.2	14.7
1/3	8.3	9	1.2	16.0	115	72	1.3	0.2	2.8	16.7	14.1
1/4	5.6	10	0.98	15.0	102	83	1.5	0.1	2.7	15.7	17.2

TABLE A-3. - ANALYSIS OF LIGNITE AFTER ION EXCHANGE FOR VARYING ACID CONCENTRATION

Particle Size Range = -10 x +48 mesh
Residence Time = 20.44 minutes
Solid/Liquid Mass Ratio = 1/2

H_2SO_4 Concentration N x 100	Ash % (MF)	Composition in MAF Coal, ppm					Composition In Ash, %				
		Na	K	Mg	Ca	Al	Na_2O	K_2O	MgO	CaO	Al_2O_3
0*	10.4	57.3	1.78	31.6	117	49.5	7.8	0.2	5.3	16.5	9.4
4.131	9.9	21	1.83	35.1	117	58.0	3.0	0.2	6.2	17.5	11.7
23.74	8.9	7	0.95	20.3	104	60.0	1.0	0.1	3.6	15.3	11.9
46.51	6.3	7.2	0.60	23.2	112	64	1.0	0.08	4.2	17.0	13.1
80.92	4.7	4.7	1.3	1.9	64	82	0.7	0.2	0.4	9.9	17.1

*Distilled Water

TABLE A-4. - ANALYSIS OF LIGNITE AFTER ION EXCHANGE FOR VARYING PARTICLE SIZE

Input H_2SO_4 Concentration = -10 x +48 mesh
Residence Time = 20.44 minutes
Solid/Liquid Mass Ratio = 1/2

Particle Size Range, Mesh	Ash % (MF)	Composition In MAF Coal, ppm					Composition in Ash, %				
		Na	K	Mg	Ca	Al	Na_2O	K_2O	MgO	CaO	Al_2O_3
-10 x +14	5.2	13	1.1	32	116	101	1.9	0.1	5.7	20.6	20.5
-14 x +20	4.6	11	1.1	16.5	96	85	1.6	0.1	3.0	14.9	17.8
-20 x +28	4.6	5	1.8	32	115	95.5	0.8	0.3	6.2	18.9	21.1
-28 x +35	5.5	7	0.92	21.3	113	94.5	0.8	0.1	3.8	17.1	19.4
-35 x +48	6.0	7	1.1	15.2	115	75.5	0.9	0.2	2.8	17.8	15.6

APPENDIX B

LIST OF SYMBOLS AND ABBREVIATIONS

SYMBOLS

δ	thickness of Nernst film, cm
$\alpha_{A/B}$	separation factor, dimensionless
φ	electric potential, ergs/coulomb
π	constant, dimensionless
υ	linear liquid flow rate, cm/sec
α	probability that a variable will exceed a certain value
ρ	density, g/cm^3
β	regression coefficient

ABBREVIATIONS

MF	moisture-free
MAF	moisture-ash-free
AA	atomic absorption
N	normal
ppm	parts per million

APPENDIX C

SAMPLE CALCULATIONS

Sample calculation to determine g/min Na^+ in a g of MAF lignite.

$$\text{g/min } Na^+ = \frac{\text{mg } Na^+/\text{kg lignite}}{\text{g sample (ash)}} \times \frac{\text{A g ash (MF)}}{\text{100 g lignite (MF)}} \times \frac{\text{B g lignite (MF)}}{\text{C g lignite (MAF)}}$$

$$\times \text{ D g/min (MAF) lignite in/out} \times \text{dilution factor} \times 10^{-4}.$$

NOTE: mg Na^+/kg lignite = ppm = 10^{-6} g Na^+/g lignite.

Since the pellet was dissolved in 100 ml solution, 10^{-6} becomes 10^{-4} during conversion from ppm to g Na^+/g lignite.

A. Before ion exchange (data from Table A-1):

$$\text{g } Na^+/\text{min} = \frac{60.24}{0.0926} \times \frac{11.35}{100} \times \frac{71.31}{59.96} \times 7.668 \times 1 \times 10^{-4} = 0.06733$$ in

B. After ion exchange for 1 minute residence time run:

$$\text{g } Na^+/\text{min} = \frac{30}{0.0930} \times \frac{6.12}{100} \times 7.668 \times 1 \times 10^{-4} = 0.01612$$ out

C. Sample calculation to find g Na^+/min in effluent for 1 minute residence time run:

g Na^+/min in effluent = mg/l(ppm) x dilution factor x solution flow rate (ml/min)

$$\times 10^{-6}$$

$$= 175.6 \times 10 \times 24.78 \times 10^{-6}$$

$$= 0.04351$$ out

D. Sample material balance closure from 100 for 1 minute residence time run:

$$\text{Material balance closure} = \frac{\text{In} - \text{Out}}{\text{In}} \times 100$$

$$= \frac{0.6733 - (0.01612 + 0.04351)}{0.06733} \times 100$$

$$= 11.4\%.$$

Calculation to find concentration of fixed ionic sodium and diffusion coefficient.

A. Fixed ionic sodium in lignite.

$$meq/cm^3 \text{ of fixed } Na^+ = \bar{C} = \frac{\rho \quad (100-W)}{100(1+Q_i-M_{ref}x0.001Q_{wt})} \quad Q_{wt}$$

where ρ = density of lignite = 1.2 g/cm^3.

W = moisture of lignite = 28.69%.

Q_{wt} = weight capacity of lignite = 1000/formula weight of carboxylic acid in lignite.

= 1000/45 = 22.22 meq/g.

Q_i = g of Na^+ in weight capacity of lignite.

= 23×10^{-3} (22.22) = 0.5111 g.

M_{ref} = atomic weight of reference ion = 1 for cation exchangers = 35.5 for anion exchangers.

$$\bar{C} = 1.2 \quad \frac{(100-28.69}{100(1+0.5111-22.22x0.001)} \quad 22.22$$

$$= 12.77 \text{ meq/cm}^3.$$

B. Diffusion coefficient in film

$$\delta = \frac{0.2r_o}{1+70r_o\upsilon}$$; where r_o = mean particle radius = 0.06809 cm

υ = throughput/ion exchange unit cross-section.

for S/L = 1/2, υ = 0.006260 cm/sec.

$$= \frac{0.2(0.06809)}{1+70(0.06809)\ (0.00626)}$$

$$= 1.338x10^{-2} \text{ cm.}$$

$$t_{\frac{1}{2}} = \frac{0.23r_o\delta\bar{C}}{DC} \quad \text{(Equation 14)}$$

$$D = \frac{0.23r_o\delta\bar{C}}{t_{\frac{1}{2}}C} \quad ; \ t_{\frac{1}{2}} = 286 \text{ seconds (Figure 2)}$$

$$= \frac{(0.23)\ (0.06809)\ (1.338\times10^{-2})\ (12.77)}{(286)\ (0.1118)}$$

$$= 8.361\times10^{-5}\ \text{cm}^2/\text{sec.}$$

Sample calculation for F test.

A. Overall F test.

H_o : $\beta_1 = \beta_2 = \beta_3 = \beta_4 = 0$ where β is a regression coefficient.

Let $\alpha = 0.10$

H_A : $\beta_1 \neq \beta_2 \neq \beta_3 \neq \beta_4 \neq 0$

F calculated = $7.832 > F_{4, 11, 0.90} = 2.54$. Therefore, reject H_o at $\alpha = 0.10$.

B. Partial F test.

H_o : the addition of x_3 to the model already containing x_1, and x_2 does not significantly improve the prediction of y.

H_A : the addition of x_3 to the model already containing x_1, and x_2 does significantly improve the prediction of y.

$$F(x_3/x_1,x_2) = \frac{SS(x_1,x_2,x_3) - SS(x_1,x_2)}{MS \text{ residual } (x_1,x_2,x_3,x_4)}$$

$$= \frac{0.793 - 0.352}{(0.094 + 0.312)/12}$$

$$= 13.0$$

$F_{1,12,0.90} = 3.18 <$ F calculated. Therefore, reject H_o at $\alpha = 0.10$.

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